The Influence of Concentration, Temperature, and Humidity on the Drying of Chinese Lacquer-Oil Varnishes

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DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE, COLUMBIA UNIVERSITY, IN THE CITY OF NEW YORK

BY

ZAI-ZIANG ZEE

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SEPTEMBER, 1925.

DEDICATED TO
MY FATHER AND MOTHER

ACKNOWLEDGMENT

The author takes pleasure in acknowledging the kindly coöperation and untiring effort of Professor Arthur W. Hixson, under whose direction this research was carried out. He wishes also to express his deep appreciation to the other members of the Faculty of the Department of Chemical Engineering, particularly to Professors Daniel D. Jackson and Ralph H. McKee for their helpful suggestions and continual encouragement.

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I. INTRODUCTORY PART

ABSTRACT

This research was planned and carried out with the object of making a systematic study of the behavior of Chinese lacquer-oil varnishes, in order to ascertain the optimum conditions under which they could be dried.

Various methods have been devised to study the drying of such varnishes under careful control of temperature, humidity, and concentration. Other factors, which seemed to have a direct bearing on the drying, were also studied, particularly the effect of viscosity and the addition of driers.

The results obtained from series of experiments have brought out new facts concerning the properties of lacquer-oil mixtures which seem to be of much importance in formulating definite specifications for the more scientific use of the materials in industry.

These facts are as follows :

1. There is a scientific basis for the mixing of Chinese lacquer with China wood oil to make different grades of varnishes.

2. There is an optimum concentration at which the mixture forms the best grade varnish.

3. There is an optimum condition of temperature and humidity under which the best film may be obtained within the shortest period of time.

4. The mechanism of lacquer drying is radically different from the process under which China wood oil dries.

5. The addition of China wood oil to lacquer in proper proportions retards the drying to some extent, and by so doing it greatly improves the quality of the lacquer film.

6. The drying of lacquer-oil varnishes may also be accomplished in the absence of moisture at elevated temperatures, the mechanism of such drying being different from that observed under ordinary conditions.

7. The viscosity of the wood oil used exerts only a slight influence on the rate of drying but it has a great effect on the quality of the dried film.

8. The addition of driers in proper amounts greatly accelerates the rate of drying, but the darkening effect of many driers prevents their use in light-colored varnishes.

INTRODUCTION

Chinese lacquer comes from the same source as Japanese lacquer, being the sap of the lac tree (rhus vernicifera). It is universally used in China as a varnish both for interior and exterior work. As a matter of fact, before the introduction of spirit- and oil-varnishes from the Occident, it was the only material used in the Orient as a protective coating for wooden surfaces.

With the exception of making lacquer-ware for decorative work, Chinese lacquer is seldom used in its pure state. It is always mixed in certain proportions with drying oils, such as perilla oil, and more frequently, with China wood oil. The oil is added not merely as an adulterant for the more expensive lacquer, but as an essential ingredient to regulate the speed of drying of the varnish and to improve the gloss and quality of the film.

Pure lacquer or lacquer-oil varnishes possess some remarkable properties not found in any other varnish. A lacquer coating is highly lustrous, and extremely tenacious and adherent to the surface. Even a very thin film shows great opacity and strong resistance to the actions of weather, moisture, and chemical reagents. No organic solvent has been found that will dissolve the dried lacquer. On account of these properties, Chinese lacquer to-day still stands foremost in the varnish industry in China.

Differing from ordinary varnishes, the lacquer-oil varnishes are mixed in the cold. The resin is always kept in liquid state. It is easy of flow and miscible in all proportions with drying oils, no thinners being necessary.

Most of the lacquer produced in China is for home consumption. Considerable quantities, however, were exported to Japan, Hongkong, Singapore, and Straits Settlements. Owing to the fact that it is somewhat poisonous to susceptible persons and that it dries too slowly, Chinese lacquer has not found a market in Europe and America. The characteristic properties of lacquer, however,

should recommend itself to wide application in the near future. For use in air-craft, Morrell[1] considered that Japanese lacquer is the best resin-oil varnish that is impervious to water. Its use could be extended to the coating of ship's bottom and the protecting of submarine cables. Its di-electric constant has not been studied, but its resemblance to vulcanite, ebonite, and bakelite, suggests the possibility of making cold-molded insulators in time to come.

The most peculiar thing about Chinese lacquer or lacquer-oil varnishes is that they dry faster in damp weather than in dry atmosphere. It is said that if the drying is hastened by means of dry air or high temperature, the film effect will be degenerated. It is therefore important to ascertain the favorable conditions under which the best results may be obtained. It is believed that researches along this line will open a new field for the scientific study of Chinese lacquer and arouse the interest of people in China engaged in the varnish industry.

1. Third Report on Colloid Chemistry, B. A. A. S., p. 107 (1920)

PREVIOUS WORK

Much has been done on Chinese lacquer and China wood oil both regarding their constitution and their individual behaviour on drying.

(1) On China Wood Oil—

After the researches of Cloez, Maquenne, Kametaka, Majima, Fahrion, Schapringer, Fokin, and others, it is now pretty well established that China wood oil consists chiefly of elaeo-stearine besides some eleine and a small percentage of glycerides of some saturated fatty acid, and that the acid obtained by saponifying the oil (viz., elaeo-stearic acid) is an isomer of linolic acid,[1] having the mass formula of $C_{18}H_{32}O_2$ and the probable constitution of

$$CH_3(CH_2)_3.CH{:}CH.(CH_2)_2.CH{:}CH.(CH_2)_7COOH.$$

(2) On Chinese Lacquer—

The formula of lacquer has not been very definitely agreed upon. Ishimatsu[2] was the first one to work on it, followed by Yoshida,[3] Bertrand,[4] Tschirch, Stevens,[5] K. Miyama[6] and others. Majima had carried out a long series of researches extending over a period of fourteen years (from 1908 to 1922), which led to the conclusion that lacquer contains urushiol (alcohol soluble), laccase (or gum and laccase), volatile matter (including moisture), and ash, and that urushiol (the most important constituent) has the mean formula of $C_6H_3(OH)_2C_{15}H_{27}$, with the two phenolic groups occupying the positions 2–3 with respect to the normal unsaturated $(C_{15}H_{27})$– side-chain.[7] The substance is not homogeneous, being

1. Ber. *42*, 674 (1909).
2. Memoirs of the Manchester Lit. and Phil. Soc., 3rd series, VII, 249 et. seq. (1882).
3. J. C. S. p. 472 et. seq. (1883); Trans. As. Soc. of Japan, XII, p. 182–222.
4. Ann. Chim. and Phy. VI, Series 12, p. 115 (1897).
5. Moniteur Scientifique, p. 731–60, (1906).
6. J. Coll. Eng. Imp. Univ., Tokyo, *4*, 89–100 (1909).
7. Ber. *55*, 172–191 (1922).

composed of at least two substances differing in the number and position of double-bonds. The presence of the phenolic groups in lacquer, as well as the peculiar nature of unsaturation being similar to that of drying oils, explains why it works very well when mixed with China wood oil. The result of such a mixture is probably condensation or even compound formation.

(3) On the Drying of China Wood Oil—

The drying of China wood oil alone has also been studied carefully by different investigators. All agreed that it dried with increase in weight. This increase was not quite uniform (14.5% according to Gardener,[1] 14.3% to 21.7% according to Weger,[2] 11.9 to 15.8% according to Meister,[3] and 11.3% according to Fahrion[4]). Owing to lack of uniformity in the samples collected and the variety of methods used in determination, there was no concurrence in any two results. The latest researches of Rhodes and Ling[5] showed that raw wood oil absorbed in 500 hours about 44% of oxygen, and that the maximum gain in weight (the maximum difference between the weight of oxygen absorbed and the amount of volatile matter given out) at the end of 250 hours was 10.5%. Meister found that wood oil absorbed less oxygen than linseed oil (about 17%). Treated wood oil absorbed more oxygen than raw oil (38% on first day and 26.2% at end of 18 days, according to Gardener). The drying of wood oil was accelerated by high temperature (Meister[6]) and retarded somewhat by damp weather (Bottler[7]). Fahrion stated that the oxygen absorption proceeded in two stages; during the first, only 4 to 6% of oxygen was taken up. The oil *appeared* dry but still remained soft and greasy. This lasted 1 to 2 days. In the second phase it absorbed the additional 8 to 10% and the film became hard and dry in 5 to 6 days.

---

1. Rep. of Sub-Committee on Paint, p. 13–14, (1911).
2. Jahres Ber. *44*, 1163, (1898).
3. Chem. Rev. F.–H.–I., *17*, 150, (1910).
4. Farben Ztg *17*, 2689 (1912).
5. J. Ind. and Eng. Chem., *17* (No. 5), 508 (1925).
6. Chem. Rev., F.–H.–I., *18*, 136 (1911); *19*, 159 (1912).
7. Chem. Rev., F.–H.–I., *19*, 265–7, 296–299 (1912).

(4) On the Drying of Chinese Lacquer—

The drying of *pure* lacquer is, in the opinion of Ishimatsu, entirely due to oxidation in the atmosphere, having nothing to do with light. The final product is oxy-urushiol. This is brought about by the aid of diastase in the lacquer (according to Yoshida and Korchelt) or by the action of acids or alkalis (according to Tschirch and Stevens). The statement of Bertrand that the drying of lacquer is due to the Mn contained in it, has been accepted with great doubt. Careful analyses carried out during the course of the present research failed to reveal a trace of Mn in the ash. Lacquer dried better in moist, than in dry air; better at ordinary temperature than at high temperature. Yoshida was the first one to carry out semi-quantitative experiments, and he found out that lacquer dried best (in 2 hours) in moist oxygen at about 20°C but did not dry at all when heated above 63°C, due probably to the inactivity of the enzymes at high temperatures. This last statement was contradicted by K. Miyama,[1] who showed that:

Heated to 70–80°C, the lacquer did not dry;
„ „ 100°C, „ „ dried after 4–5 hours;
„ „ 150°C, „ „ dried after 30 minutes;
„ „ 180°C, „ „ dried after 10 minutes.

This indicates that the drying of the lacquer does not depend entirely on the enzymes, but at high temperatures, the quick removal of volatile matter hastens the oxidation. No mention, however, was made with regard to the condition of humidity under which the sample was dried.

So far, no experiments have been carried out on the drying of lacquer-oil mixtures under regulated conditions of concentration, temperature, and relative humidity.

1. Chem. Rev., F.-H.-I., *15*, 148–9, (1908).

SCOPE OF RESEARCH

The scope of the present research was confined chiefly to the study of the three conditions influencing the drying of lacquer-oil varnishes, namely, concentration, temperature and humidity. The effects of viscosity and of driers were also studied because they seem to be closely related with the present subject.

In the *choice of materials*, several samples of Chinese lacquer and of China wood oil were examined qualitatively, and the sample that gave the best results in the preliminary examination was used.

With regard to *concentration*, a set of lacquer-oil mixtures was carefully prepared, with concentrations ranging from 0% lacquer to 100% lacquer.

Referring to *temperature*, 25°C, 40°C and 0°C were chosen to represent ordinary room temperature, hot summer, and cold winter, respectively. For drying at 0% relative humidity, 60°C, 80°C and 100°C were also used.

As to *humidity*, five degrees of saturation were taken, viz., 0%, 40%, 60%, 80% and 100% relative humidity. At 20% relative humidity, the results were found by preliminary test to differ little from 0% relative humidity, and therefore no quantitative experiments were carried out.

It was also found necessary to limit the *time* for drying. Each set under one particular condition was given one week to dry. Samples found sticky or "wet" at the end of that period were considered "non-drying."

This research did not attempt to make a comprehensive study of the composition and constitution either of China wood oil or of Chinese lacquer. Only those chemical and physical properties that seemed to have a direct bearing on the drying of the varnishes were examined, mainly for the purpose of specification.

Nor did this research include the study of the action of pigments added to the varnish; nor of the reaction taking place between Chinese lacquer and the different chemical reagents, both inorganic and organic; nor of the other interesting phases, such as di-electric constant, vulcanization, etc. Some of these topics have been studied with care by early investigators, while others are still open for future research.

II. EXPERIMENTAL PART

SPECIFICATIONS OF MATERIALS USED

1. Chinese Lacquer:

The lacquer used in this research was of the highest grade and purest quality obtainable in the market. It was bought from one of the well-known varnish companies in Shanghai,—the Hoong Nion Chinese Paint and Varnish Manufacturing Co., 76–77 Kiukiang Road, Shanghai, China, and was shipped directly to this Laboratory in sealed bamboo tubes. It was an easily flowing liquid, somewhat like the rubber latex but of a greyish color which rapidly turned black on exposure to the air. Extraction with absolute alcohol, followed by filtration and washing, yielded the following results which represented the mean of two analyses :—

Part soluble in absolute alcohol	57.48%
Part insoluble in alcohol { gum 8.55 / res. 2.79 } ...	11.34
Water and Volatile Matter (by diff.)	31.18
	100.00%

This agreed very well with the results obtained by Ishimatsu, as follows :—

Part soluble in alcohol	58.24%
Gum	6.34
Residue.....	2.24
Moisture and Volatile Matter (by diff.) ...	33.18
	100.00%

Organic combustion of the alcohol-soluble portion or *urushiol* (dried to constant weight at 100°C) showed that it contained :

C	70.22%
H	8.41
N	0.00
Ash	.25

It will be seen that the results obtained were not far off compared with the analyses made by Tschirch and Stevens in 1906, thus,

C	72.03%	being average of 8 samples analysed.
H	8.64%	
N	1.05%	
Ash	.64%	

The nitrogen contained in the original lacquer, as determined by Kjeldahl's method, was small in quantity, being only 0.30%.

Urushiol is not a pure compound, but "a mixture of at least two compounds with isomeric side-chains which appear to include several unsaturated complexes."[1] The fact that it contained two phenolic groups[2] and that one of these groups is more readily methylated than the other,[3] at once suggested the possibility of determining its average formula weight by using Morgan and Meighan's method.[4] This was carried out, which gave the following analytical data:—

T = 26.7°C = 299.7°(Abs.)
Bar. Pres., 29.77 inches or 756.16 mm.
V. P. of Toluene ..... 32.00 mm.
True Pressure ..... 724.16 mm.

	(I)	(II)
Weight of Sample	401.8 mg.	530.5 mg.
V_t	10.2 cc.	13.4 cc.
V_o	8.85 cc.	11.6 cc.
Sodium Hydroxide Equivalent	0.0784	0.0780
Formula Weight	510	513
Mean.....	512	

1. Majima: "Oxidation of Urushiol-di-methyl-ether with Ozone," Ber., *42*, 3664–73, (1910).
2. K. Majima: J. Coll. Eng. Imp. Univ. Tokyo, *4*, 89–100 (1909).
3. Majima and Takayama: "Mechanism of Oxidation of Urushiol," Ber., *53*, 1907–16 (1920).
4. Ind. and Eng. Chem., *7*, No. 6, 626, June, 1925.

This agreed very well with Miyama's empirical formula, $C_{34}H_{50}O_4$ (F. W. = 522), showing that the lacquer used in the present research differed little from that used by previous investigators.

2. China Wood Oil:

The raw oil used was obtained from Gilespie & Co., of New York, marked Expeller Oil (i. e., oil expressed from Chinese nuts in the Anderson Expeller). The physical constants were determined as follows:

Color	light yellow
Specific Gravity (15.5°C)	0.9392
Refractive Index (22°C)	1.5185
Dispersion Value (22°C)	.02081
Acid Number	16.65
Iodine Number (Wijs)	166.3
Heat Test (Brown's)	11¾ minutes

The bodied oil was prepared by heating 2000 cc. of the raw oil in a large beaker (insulated by asbestos and covered with a perforated watch glass) to 215°C during one hour, and maintaining the temperature at 215-220°C for 1½ hours. The oil was allowed to cool to room temperature and aged for one week before mixing with lacquer. It was found that bodied oil prepared in this way had about the same viscosity as pure lacquer and mixed with it very well.

In the following experiments, where the term "oil" is used alone, it is meant for "bodied China wood oil," unless otherwise specified.

3. The Lacquer-oil Mixtures:

150 grams each of nine samples whose lacquer concentrations ranged from 10% to 90% were prepared by mixing proper proportions of the two ingredients at room temperature, and triturating in a small glass mortar for exactly 5 minutes. The varnishes so prepared were immediately turned into round, seamless, tin cans, provided with tight-fitting covers. On the surface on the varnish was placed a circular oil paper[1] so that

1. This is the usual practice in China for preserving lacquers.

there would be neither surface oxidation nor volatilization. For brevity, the term "lacquer-varnishes" are used in the following pages for such mixtures.

4. Driers :

The powdered drier used was litharge, containing about 93% of lead.

The metal content of the paste and liquid driers[1] was ascertained by analysis to be as follows :

Cobalt Linoleate (liquid).....1.50% Co.
Manganese Linoleate (paste) .....2.43% Mn.

Both linoleates were kept in air-tight containers until use.

---

1. Furnished by courtesy of Toch Brothers, Long Island City.

INFLUENCE OF VISCOSITY ON DRYING

(I) Measurement of Relative Viscosity

The importance of viscosity in different kinds of varnishes as a determining factor for their quality is being more and more definitely recognised. The lack of a suitable instrument for determining the absolute viscosity of varnishes in general, makes it extremely difficult to secure satisfactory results. To study the behavior of one kind of varnish under varying conditions, relative viscosity is sufficient, but it must be measured with reasonable degree of accuracy. The commercial viscosimeters in general use are constructed either on the principle of the rate of flow of the liquid or on the principle of the resistance offered by the liquid to the motion, tortional or in a straight line, of a body propelled by some known force. Of the first type may be mentioned the well-known Oswald, the Saybolt, the Redwood, and the Engler Viscosimeters. Although differing a little in their construction, nearly all of them determine the viscosity of a liquid or semi-liquid by the rate of its flow through a capillary tube or a small orifice at standard temperatures. The type represented by the MacMichael Viscosimeter uses a revolving disc or bob hanging in a liquid on a standard wire, the viscosity being measured by the amount of torsion produced in the wire as indicated on the graduated disc. Various substances have been used as standards, water for light liquids, and glycerine, sugar solution or rape-oil for heavy ones.

None of the above mentioned types proved to be suitable for determining viscosity in this research. The varnishes used were heavy in consistency, opaque in color, and having viscosities varying widely at different concentrations and temperatures. When the first type was used, the liquid was too thick to go through the capillary tube or the small orifice within the experimental period. Moderate heating reduced the viscosity but changed the composition of the varnish. The MacMichael Viscosimeter was also tried

and found unsuitable, because (1) the surface of the varnish rapidly thickened on exposure when the disc was being rotated and (2) several wires had to be standardized to cover the range of viscosity.

The bubble test, widely used in the varnish industry, depends on the rate at which an air bubble rises through a narrow tube of liquid. The so-called "R. P. C." Viscosity Tubes (devised by R. P. Cargille of New York) are claimed to have their inside diameters measured with a device indicating variations of 1/100 mm. through the entire length of the tube, which is about 11 cm. While such tubes were useful in making rough and rapid determinations of viscosity, they failed to give satisfaction when greater accuracy was demanded. The viscosimeter devised by Victor R. Abrams, Joseph T. Kavanagh and Charles H. Osmond[1] known as the Atreco Viscosimeter, has a special device to control the size of the air bubble at given temperature and is provided with two etched marks along a narrow shaft, so that readings may be accurately made. This last type likewise gave no satisfactory results with varnishes having a dark color and adhering tenaciously to the walls of the tube.

The type of viscosimeter which fulfilled the requirements of the work on lacquer-varnishes was a modification of the form described by Holde-Mueller[2] and used the principle of the falling weight. By means of this type, the absolute viscosity of any liquid, light or heavy, transparent or opaque, may be obtained from Stokes's Law :

$$u = \frac{2r^2g\ (s\text{-}m)}{9\ n}$$

where u is velocity of fall

r is radius of sphere

g is acceleration of gravity

s is density of sphere

m is density of the material under examination

n is its viscosity.

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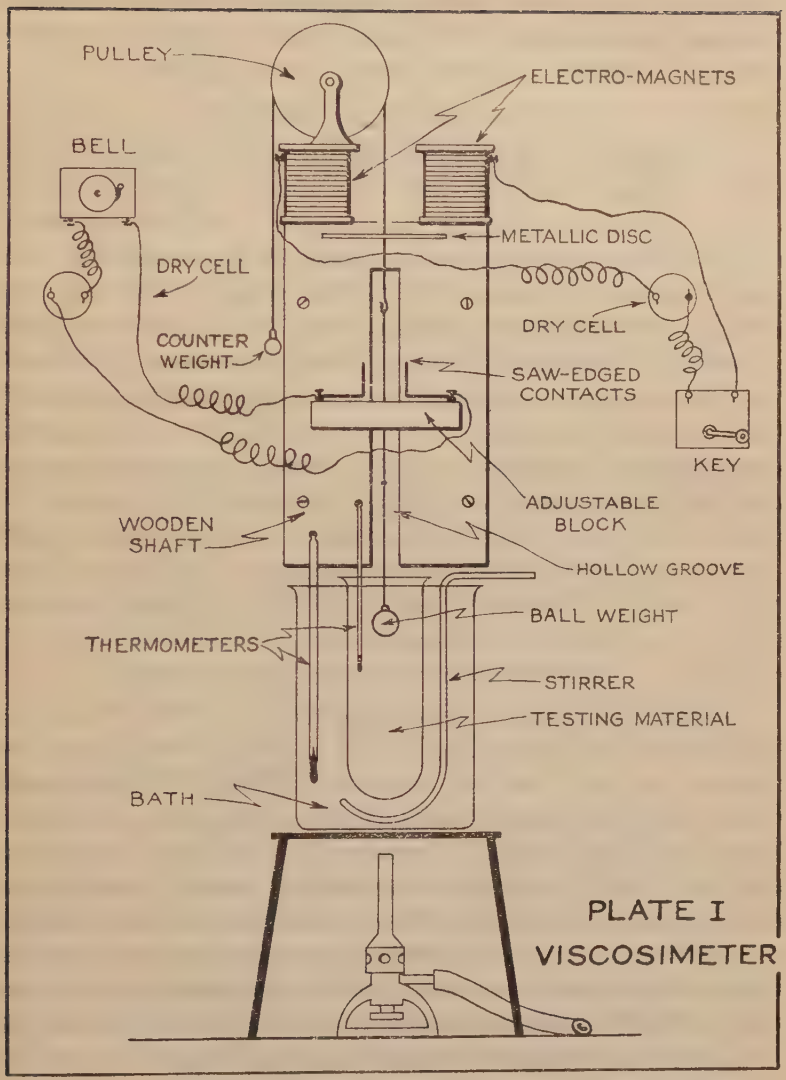
1. Chem. and Metal. Eng., Oct. 5th, 1921.
2. "Hydrocarbon Oils," 2d. ed. p. 10 et seq.


PULLEY
ELECTRO-MAGNETS
BELL
METALLIC DISC
DRY CELL
DRY CELL
COUNTER WEIGHT
SAW-EDGED CONTACTS
KEY
ADJUSTABLE BLOCK
WOODEN SHAFT
HOLLOW GROOVE
BALL WEIGHT
THERMOMETERS
STIRRER
TESTING MATERIAL
BATH
PLATE I
VISCOSIMETER

It is also easy to express the viscosity in terms of Saybolt seconds or centi-poises by standardizing the velocity of the ball against a Saybolt or MacMichael Viscosimeter. This, however, was found unnecessary in the present research, which only called for the *relative* viscosity of the same varnish at different temperatures, or of different varnishes at the same temperature.

(II) Description of Apparatus

A detailed sketch is given on Plate I. The ball used was of steel, weighing 8.2 grams, while the counter-weight weighed 7.4 grams. The distance of fall was 10.5 cm. The tube containing the liquid was 15.5 cm. long and 4 cm. in internal diameter and had a capacity of about 125 cc. The weight of the ball, the volume of the tube, and the distance of the drop could all be varied to suit the experimenter. But the difference between the ball and its counter-weight had to be such as to keep the wire taut when the disc was released from the electro-magnet. The wire for suspending the weights was a very fine steel wire passing through a frictionless pulley provided with ball bearing. The diameter of the tube was such as to allow the ball to travel through the liquid perpendicularly without touching the sides at any place. The bath could be heated by a flame or cooled by running water or ice. A very sensitive thermometer reading to 1/5 of a degree (C) was used as a small stirrer for the liquid inside the tube.

When the material being tested had acquired the desired temperature, the current on the electro-magnet was broken by pushing the key. The ball then traveled freely downwards until the metallic disc touched the saw-edged contact on the adjustable block, closing the circuit and causing the bell to ring. Instead of an electric clock, a stop-watch was used for timing. It was found that readings to the nearest fifth of a second were accurate enough to yield distinct values for plotting points on the curves and to make comparisons with varnishes at the temperature range between 0°C and 60°C. This temperature range was chosen, because the lacquer decomposes above 60°C and congeals below 0°C.

When the temperature was kept constant, duplicate readings were made until they checked within one-fifth of a second. When determinations were made in rapid successions, with change of

temperature, two sets of readings were made, one with rise and the other with fall of temperature, and the average of two readings at the same temperature was taken. It was found that where the temperature did not change too rapidly and the liquid was thoroughly stirred, readings did not differ more than two-fifths of a second, generally less. To eliminate any initial pressure due to the weight of the column of the liquid, the tube was adjusted every time so that the upper surface of the liquid was just tangent with the top of the ball when the disc was held by the electro-magnet.

The viscosimeter was run against C. P. glycerine (sp. gr. 1.26) for comparison. It was found that, with the arrangement described above, the time for the fall of the ball through glycerine was exactly one second at 15.0°C and 3.4 seconds at 0°C.

The special features in this modified form of viscosimeter are these:

(1) The substitution of the electric bell for the electric clock reduced the cost without sacrificing the required degree of accuracy.

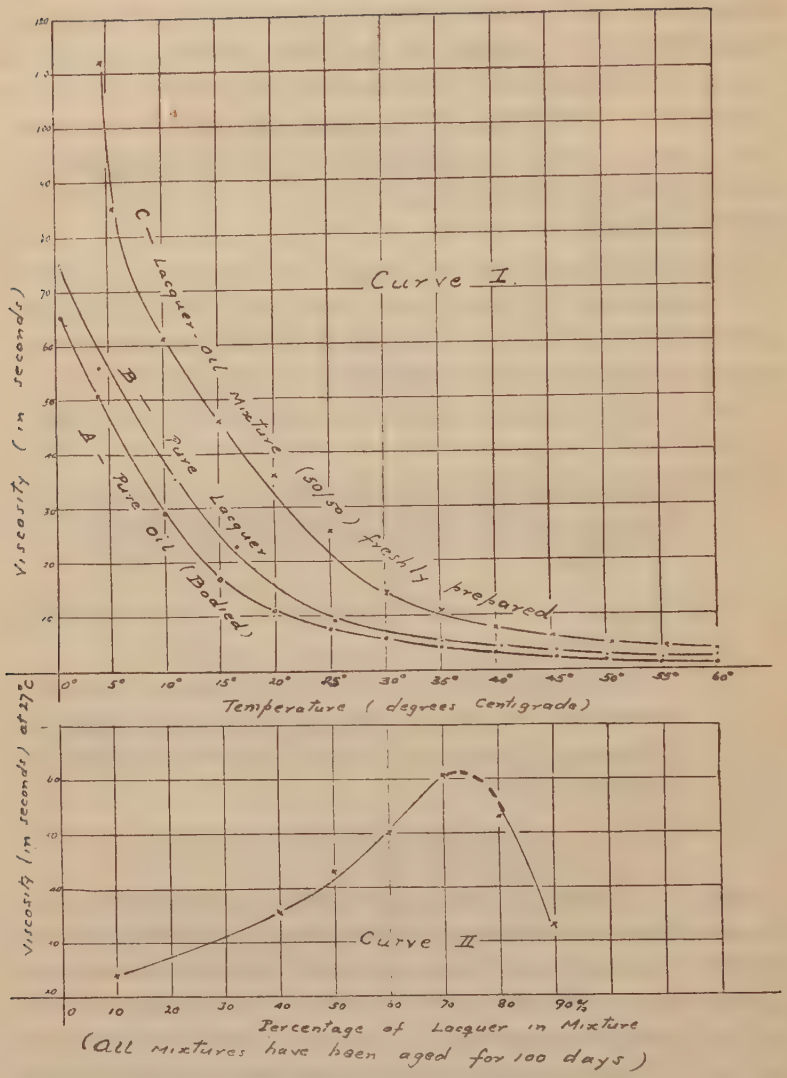
(2) The circular disc and the saw-edged conductors insured good contact.

(3) The adjustable block enabled determinations to be made within wide ranges of viscosity, by simply varying the distance of fall and the length of the tube containing the liquid to be tested.

(III) The Temperature-Viscosity Diagram

Seaton, Probeck and Sawyer[1] studied the viscosity of various varnishes that have been mixed with thinners, and they found by Doolittle's method that the temperature-viscosity diagram was a curve if the varnish was in true solution, but a straight line if it was in a state of suspension. Where no thinners are used, as in the case of lacquer-varnishes, Seaton's explanation evidently does not apply, because smooth curves were obtained in this experiment

1. J. Ind. & Eng. Chem., 9, 35 (1917).


Curve I.
C — Lacquer-Oil Mixture (50/50) freshly prepared
B — Pure Lacquer
A — Pure Oil (Boiled)
Viscosity (in seconds)
Temperature (degrees Centigrade)
0° 5° 10° 15° 20° 25° 30° 35° 40° 45° 50° 55° 60°
Curve II
Viscosity (in seconds) at 27°C
Percentage of Lacquer in Mixture
0 10 20 30 40 50 60 70 80 90%

(All mixtures have been aged for 100 days)

for pure wood oil, for pure lacquer, and for fifty-fifty mixture. It is not likely that the lacquer would form a true solution with bodied wood oil especially at ordinary temperatures, as microscopic examinations of the fifty-fifty mixture revealed small globules of oil uniformly dispersed throughout the dark-colored lacquer.

In Experiment I, pure lacquer and bodied wood oil were used. The mixture consisted of half lacquer and half wood-oil stirred thoroughly by means of a horn spatula for 10 minutes. The results are shown in Table I and graphically represented by Curve I.

TABLE I

Viscosity (in seconds)

Temperature	*A (Pure Oil)*	*B (Pure Lacquer)*	*C (Mixture)*
0°C.	...	75.0	...
1	65.3	...	...
4	...	56.4	...
4.5	51.0	...	112.6
6	...	...	85.2
10	29.7	...	61.4
11	...	35.4	...
15	17.1	...	46.1
15.5	...	29.4	...
20	11.4	15.8	36.0
25	7.8	...	25.7
25.5	...	9.2	...
30	6.2	...	14.0
31	...	5.5	...
35	4.4	4.5	10.8
40	3.2	...	7.8
41	...	4.2	...
45	...	...	6.2
46	2.2	3.3	...
50	1.9	...	...
51	...	3.0	4.8
55	1.4	2.7	4.2
60	1.1	2.5	3.5

It will be seen from Curve I that the viscosities of all three samples increased *very rapidly* with fall of temperature. This is usually the case with heavy vegetable-oils, and oil mixtures. If the lacquer-oil varnish were a mere suspension, the resulting viscosity would be that of the dispersion medium,[1] viz., one of the two ingredients. If it were a solution, the curve would lie somewhere between the two original curves. But, as C (Curve I) lay above A and B (with viscosities greater than the sum of the two) and as it assumed the same shape as the other two (almost parallel to them), there is good reason to believe that the resulting substance was an emulsion.

From the experiments on drying, it was found that in most cases the mixture containing 80% lacquer and 20% oil gave better results than any other mixture. It generally dried better and formed a more homogenous glossy film. From theoretical considerations the best composition ought to be the one where emulsification is most complete. If it were so, it would show up in the viscosity-concentration diagram.

(IV) The Viscosity-Concentration Diagram

Experiment II was carried out by using mixtures of varying concentrations (from 10% lacquer to 90% lacquer) which had been prepared from the same ingredients as were used in Experiment I and aged for 100 days. The determinations were made at 25.5° C., with results as follows :

Table II

Concentration	*Viscosity* (*in terms of seconds*)
10% lacquer	24.0
20% lacquer	38.7*
30% lacquer	32.3
40% lacquer	35.4

1. Taylor's Colloidal Chemistry, p. 21–22.

* The abnormally high viscosity of the 20% composition is due to oxidation into a black viscous substance when the paper cover was found to be not in close contact with the surface.

50% lacquer 45.4
60% lacquer 50.0
70% lacquer 60.6
80% lacquer 53.6
90% lacquer 33.0

These values were plotted on Curve II. While the 80% composition did not exactly come to the peak of the curve as expected, the nature of the curve showed that the general assumption was in the right direction. It is likely that the best emulsified mixture was neither 80% lacquer nor 70% lacquer (which had the highest value in the present experiment) but had a composition somewhere between the two, as indicated by the dotted line on the curve. It is not improbable that with compositions varying from 71% to 79% lacquer, such an optimum concentration may be found which will occupy the peak on the curve. This was not attempted, because the mixtures used had been aged for 100 days, and it was impossible to duplicate exactly the same conditions unless the whole series was prepared at the same time.

These experiments on viscosity, therefore, showed that China wood oil forms an emulsion with Chinese lacquer, and that the best emulsified mixture makes the most satisfactory varnish.

Emulsions increase enormously in viscosity with ageing. A comparison of the values on the tables will verify the statement, for, while a freshly prepared 50/50 mixture gave a viscosity of 25.7 seconds at 25° C., the same mixture which had been aged only for 100 days gave a value almost double as much, viz., 45.4 seconds at 25.5° C.

It then seemed advisable to find out what effect the viscosity of the China wood oil had on the resulting lacquer-mixture. For this purpose, four samples of the same oil (graded according to their viscosity) were taken, one raw, and the other three bodied at 215–220° C. for different lengths of time so that their relative viscosities were approximately 1 : 2 : 8. Thus,

Oil	*Grade*	*Viscosity R.P.C. at 25° C.*	*Refractive Index at 25° C.*
No. 1	Raw	(3.8) sec.	1.5178
No. 2	Bodied	18.8 sec.	1.5115
No. 3	Bodied	36.4 sec.	1.5100
No. 4	Bodied	147.4 sec.	1.5095

Each sample of oil was mixed with 80% of lacquer at room temperature, triturated in a small glass mortar for about five minutes, covered with paper and aged for one week before use. Clean plates were then coated with the mixtures as usual and dried in a ventilated oven at 22 25° C. and 65–75% relative humidity. Plates were weighed at regular intervals when the condition of drying was likewise observed. The results are tabulated as follows :

TABLE III

Plate	*Sample & Wt. (20% Oil)*	*Percentage Decrease in Weight after (days)* ½	1	2	3	4	5	6
10	No. 1— 57.3 mg	1.9	2.4	2.8	3.0	2.8	...	...
11	No. 1— 67.7 mg	2.5	...	...	...	...	...	...
12	No. 2— 98.1 mg	5.8	6.3	...	6.4	6.5A	6.3	...B
13	No. 2—105.5 mg	6.4	...	...	6.5A	6.2	...B	...
14	No. 3—135.7 mg	9.8	9.9	9.6	...A	9.5	...B	...
15	No. 3—115.8 mg	7.7	7.8	...	7.9A	...	7.8B	7.7
224	No. 4—125.6	10.0	...A	...	10.1B	10.2	...C	...
225	No. 4—198.1	12.4	...A	12.7	...B	12.6	...C	...

Plate	*8*	*10*	*12*	*16*	*20 days*	*Final Condition*
10	...	...	...	2.6	...	No signs towards drying
11	...	...	2.1	2.2	...	Ditto
12	...	...	...	5.8	...	Still tacky
13	...	...	...	5.7	...	Ditto
14	...	...	...	9.4	...	Ditto
15	...	...	...	7.3	...	Ditto
224	...	...	...	10.4	...D	Very slightly tacky
225	...	...	...	12.2	...D	Ditto

NOTE:—The dotted line indicates that the weight taken at that particular period shows no change over the previous period.

A—beginning to dry
B—still quite sticky
C—very slightly sticky
D—dry to touch

The above table shows that raw oil added to lacquer retarded its drying. This action seemed to be mutual, the lacquer preventing the oil from absorbing oxygen and the oil containing a large amount of substances not easily volatile at room temperature, acting as a protective coating and inhibiting the escape of volatile matter from the lacquer. Consequently, very slight change was observed, both in weight and in appearance. It is likely that lacquer formed only a loose suspension in raw wood oil, as shown by lack of uniformity of dispersion when examined under the microscope.

Bodied oil formed a more homogeneous mixture with lacquer, and within certain limits it appeared that the more viscous the oil, the better emulsion it made with lacquer (80%). Therefore, the mixture containing the most viscous oil was almost dry to touch in 20 days, while the other two were still slightly tacky. It may also be seen that the higher the viscosity of the original oil, the greater the percentage loss of weight both in ½ day and at the end of 20 days. As the more viscous oil itself contained less volatile matter, this excessive loss of weight could only come from the lacquer. The drying of lacquer (or of mixtures containing high percentages of lacquer) is, therefore, quite different from the process under which pure wood oil (raw or bodied) dries. The former is accomplished chiefly by the formation of intermediate products which escape constantly, while the latter is due to oxidation rather than to volatilization.

To prove this, another series of experiments was undertaken, using pure wood oil dried side by side with lacquer mixtures.

TABLE IV

Plate	*Sample of Oil*	*Weight*	*Increase in Weight after :*			
			10	*12*	*16*	*20 days*
226	No. 1	76.8	1.0	1.5	1.6	7.0
227	„ „	55.5	1.0	1.7	1.8	6.5
228	No. 2	132.3	0.7	...	...	6.5
177	„ „	89.0	1.0	3.2	6.6	7.6
180	No. 3	114.6	0.2	1.1	1.4	4.4
171	„ „	109.0	0.5	1.0	1.1	4.7
172	No. 4	150.1	0.2	0.8	0.8	2.7
173	„ „	146.5	0.4	0.8	0.9	4.5

NOTE:—Practically no change in weight was observed during the first ten days.

The raw oil dried flat at the end of ten days; bodied oil (No. 2) dried with an opalescent appearance in 12 days; while the other two samples did not dry even at the end of twenty days. Nearly all of them dried with increase of weight, due to absorption of oxygen from the air. Raw oil was less saturated than bodied oil, as shown by their refractive indices; so it absorbed oxygen more readily, and dried more quickly. According to Meister[1] the net increase at the stage of final drying will be the same in all samples, if exposed long enough.

Microscopic examination of pure oil films (that dried flat) revealed characteristic wrinkles which were well marked. These wrinkles were finer and finer, as the oil used became more and more viscous. The film formed from bodied oil of medium viscosity showed only a few cracks; while that of a highly viscous oil that dried slowly, was perfectly transparent and homogeneous. This was also the case with raw oil that dried quickly at 100° C. and zero humidity. The wrinkles were then due to too rapid absorption of oxygen from the air along with some moisture which was enveloped by the dried oil film on the surface and could not escape. So the film "swelled up." Where moisture was absent and where oxidation was slow enough to allow the escape of moisture, the film did not "swell up" but dried with a gloss.

The dry, tight film formed by pure lacquer, especially in humid air, suggested that lacquer did not "swell up" on drying but shrank when intermediate products were formed. The process is just the reverse of that of the oil. This leads to the conclusion that oil and lacquer, when mixed in proper proportions mutually improve the quality of the film. The oil imparts a high gloss to the dull dry lacquered surface. And the "shrinking" effect of the lacquer counteracts the "swelling" of the oil film, producing in moist air a continuous, smooth film even on quick drying. A film containing as low as 20% of lacquer and dried at room temperature on long exposure to saturated moist air showed under the microscope such an effect, perfectly homogeneous and absolutely free from wrinkles.

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1. Chem. Rev.—Fett.-u-Harz Ind. (1911) page 136.

Conclusions on Viscosity

The experiments on viscosity showed :

(1) That China wood oil forms an emulsion with Chinese lacquer,

(2) That the best varnish is the mixture where emulsification is most complete,

(3) That the more viscous the bodied oil to mix with the lacquer, the better it dries, and the firmer and more homogeneous the film becomes, and

(4) That China wood oil and Chinese lacquer, when mixed in proper proportions, mutually improve the quality of the film, the oil imparting a gloss to the film, while the lacquer counteracts the " swelling " effect of the oil by the " shrinking " power of its own.

THE DRYING PROPER

DISCUSSION OF APPARATUS AND PROCEDURE

Various types of humidifiers and dehumidifiers are in the market. Most of them proved to be unsuitable for the drying of lacquer-varnishes in this research. J. A. F. Wilkinson[1] suggested passing air from a "blower," saturating it with moisture at the temperature of the water, and calculating the relative humidity in the drying tube from the pressure of water vapor and the known temperature of the tube. Unless the air is forced very slowly through long columns of wet broken glass or through a chamber provided with an efficient spray system, it is doubtful if the air from the "blower" is saturated. The same author also suggested that 'it should be possible to vary the degree of humidity, if required, by passing the air through sulphuric acid of known strength or by mixing it in known proportions with dry air.' This seemed more practicable for the present purpose. The following apparatus was devised, utilizing these principles.

(A) Apparatus for Drying Lacquer at Ordinary Temperatures

Plate II shows the construction of an apparatus which was developed for this purpose and which proved to be satisfactory. Its essential features are :—

(1) A means of mixing the moist and dry air in proper proportions to give the required humidity at given temperatures,

(2) A means of bringing the mixed air to the desired temperature, and

(3) A means of measuring and checking the degree of humidity quickly and accurately at any time.

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1. Journal of the Oil and Color Chemists' Association, Vol. VII, No. 53, p. 239, Nov. 1924.

(1) To obtain a proper mixture, the air from one direction was dried by passing it through two concentrated sulphuric acid jars and two calcium chloride jars in the order shown. The advantage of using both sulphuric acid and calcium chloride is obvious. Most of the drying (or dehydration) was done in the first acid jar which also indicated the rate of flow of the incoming air. The remaining moisture was taken up by long columns of calcium chloride of four mesh size. When the bottom of the calcium chloride jars gathered a little moisture, the acid in the first jar was quickly renewed. The last jar containing also sulphuric acid served the double purpose of removing the last trace of moisture and of acting as a bubble counter. This enabled the operator to make sure that the rate of flow was uniform throughout the train. This constituted the "dehumidifier."

The "humidifier" consisted of a tall jar filled with glass beads (or capillary tubing) through which the air coming from another direction slowly ascended. The height of the water column in the jar varied with the pressure required for each experiment. The whole was immersed in a temperature considerably higher than that of the drying chamber. The most convenient way was to keep the bath at 95°-100°C. by bubbling live steam through it. The air then went through a moisture trap immersed in a bath at the same temperature as the drying chamber, so that excessive moisture was condensed.

The mixing of the two currents of air was easily accomplished by means of a T-tube. The flow of each current was regulated by means of a screw clamp attached near the inlet. It is important that the *total* volume of mixed air going over in unit time should always be constant, otherwise the indications on the wet-bulb thermometer (see below) would not mean anything. This rate depends on the size of the chamber and that of the indicator bottle, and can only be ascertained by trial. If the velocity of the current is too high, a draft would be created. If too low, there would not be enough ventilation to remove the moisture evaporated from the wet bulb. Experiment proved this to be true. Once the proper rate was found, that rate was maintained

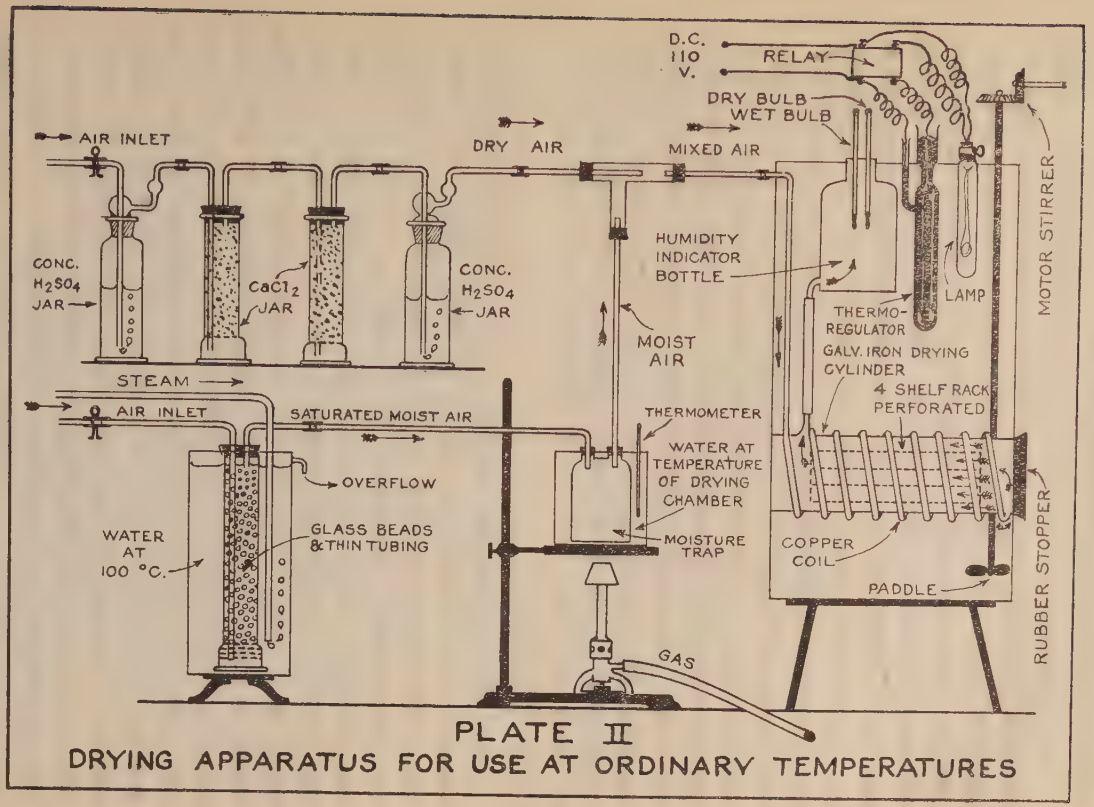


PLATE II

DRYING APPARATUS FOR USE AT ORDINARY TEMPERATURES

as constant as possible throughout the whole series of experiments. In the present case, it was found that a flow of 200 cc. of air per minute gave the most satisfactory results.

(2) *Temperature of the air.* The air was brought to the desired temperature by forcing it through a tortuous copper coil, about 15 feet in total length, surrounding the drying chamber or cylinder. Air entered the chamber from the bottom of one side and issued at the top of the other. The chamber and the coil were both immersed in water at the desired temperature, which was controlled by a lamp, a relay and a mercury thermo-regulator. The chamber was made of galvanised iron, about 10″ long and $2\frac{1}{2}$″ in diameter, with one end protruding a little and closed by a large rubber stopper, to facilitate the quick removal and replacing of samples with as little disturbance to the equilibrium of the chamber as possible. Glass plates, 1″ x 3″, which were coated with lacquer mixtures and carefully weighed, were placed on a perforated rack in two rows of four shelves each. Each rack could accommodate 24 plates at a time. Air circulated freely and evenly over the surface of these plates.

(3) *The "Humidity Indicator."* The commonest and most accurate way of measuring relative humidity is the well-known "wet-and-dry-bulb method." Many experimental difficulties were encountered in measuring the humidity. If the wet bulb were introduced into the chamber, it would soon saturate the small enclosed space with moisture, unless a rapid current of air was forced through to ventilate it. This latter condition, however, would not truly represent the ordinary atmospheric condition outdoors. To eliminate these difficulties, an indicator bottle was placed directly above the chamber to receive the issuing air. The mouth of the bottle had to be large enough to effect the rapid removal of moisture evaporated from the surface of the wet bulb, but small enough to prevent the surrounding air from rushing in. To approximate the conditions in the chamber as nearly as possible, the diameter of the indicator bottle was about the same as the cylinder. No water reservoirs of any sort were used, the wetting of the bulb being done by placing a drop of water on the wick from time to time. It was unnecessary that the dry

and the wet bulb should both be placed inside the indicator bottle as shown in the diagram. The "dry-bulb" may be immersed in the bath which necessarily had the same temperature as the cylinder or drying chamber.

The bath was a tall cylinder of galvanised iron about 12″ high and 9½″ in diameter. Water which almost reached the brim of the tank was heated and its temperature regulated electrically. The stirring was done by a small motor stirrer of adjustable speed. The cylinder was covered with asbestos sheeting to prevent radiation.

(4) *Testing the Efficiency of the Apparatus.* The apparatus was first tested out by passing through the system a current of air of known humidity and comparing it with the readings on the thermometers. By this means, it was found that for relative humidities higher than 20%, the readings checked fairly well. For lower humidities, it was difficult to obtain good readings unless the air current was very swift. The reason for this has been given above.

A more accurate way of testing the apparatus was to allow it to run for one half hour until equilibrium was established in the system. The readings of the dry and wet bulb were taken and the relative humidity recorded. The wet-bulb thermometer was then removed from the indicator bottle, and replaced by a 1-holed rubber stopper carrying a short glass tube and a rubber tube which led the issuing air through three weighed U-tubes (glass stoppered) containing phosphorus pentoxide. The volume of the issuing air was measured by a carefully calibrated gasometer, consisting of a tall cylinder of 20-litre capacity and reading to the nearest 10 cc. The meter was water sealed. But as there is a set of weights to keep the enclosed air at atmospheric pressure, the partial pressure of water-vapor in the cylinder could be neglected. 18,530 cc. of air were collected at room temperature in about 90 minutes. The U-tubes were quickly removed, stoppered, and weighed. In each case the mean of two close values was taken to calculate the relative humidity and to compare it with that obtained from the readings of the wet- and the dry-bulb. Thus.

Test	*Temp.*	*Total H_2O*	*Mean*	*Relative Humidity*		
				Calc.	*Recorded*	*Deviation*
1	25°C	.0505 g	.0537g	12.7%	20%	7.3%
2	,,	.0569				
3	,,	.1535	.1550	36.8%	40%	3.2%
4	,,	.1565				
5	,,	.3296	.3300	78.0%	80%	2.0%
6	,,	.3304				
7	40°C	.3690	.3715	37.7%	40%	2.3%
8	,,	.3740				
9	,,	.7692	.7670	77.8%	80%	2.2%
10	,,	.7648				

It will be seen that at 25°C, the deviation becomes smaller as the relative humidity is increased. At 40°C, this deviation is fairly constant (about 2%). Exact adjustments may be made either by making due allowance for the amount of deviation or by extrapolating the true value of relative humidity from the curve plotted. As atmospheric humidity easily changes within a few per cent even on the same day, it seems sufficient to take the round numbers as recorded.

(B) Apparatus for Drying Lacquer at 0° C

When the temperature approached the freezing point of water, the " dry-and-wet-bulb method " as described above failed to indicate even approximately the relative humidity of the air current. This was because at very low temperatures the space in the indicator bottle was very easily saturated with moisture even by the introduction of a tiny drop of water on the wick of the wet bulb, unless the air current traveled at an enormous speed. It was likewise difficult to supercool the water on the wet bulb much below 0° C. without causing ice to be formed around the wick. Once crystallization took place, the wet-bulb temperature either stood still or even rose instead of going down. For these reasons, true indications of relative humidity could not be obtained by using the above apparatus.

Another method was devised using sulphuric acid of various concentrations having vapor pressures corresponding to those of

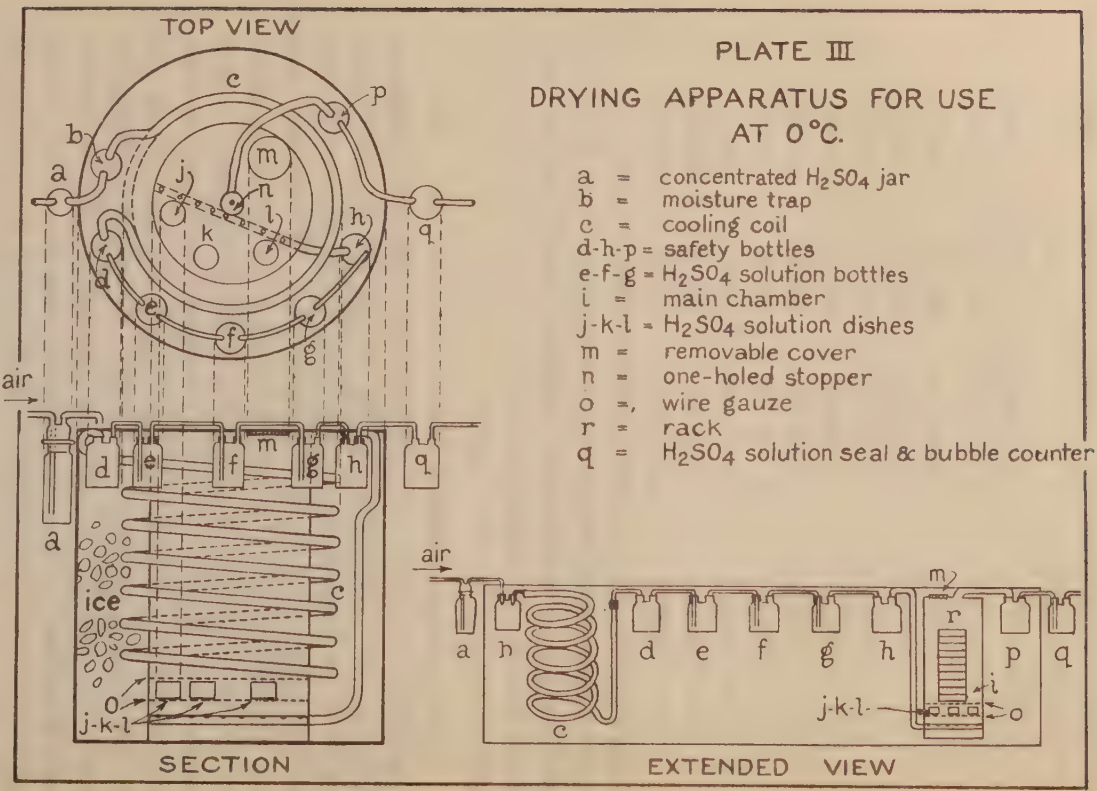
water vapor at given temperatures and given humidities. A whole series of such concentrations has been worked out by different investigators, and tabulated by Robert E. Wilson[1] as given below:

Relative Humidity	*Concentration of H_2SO_4 required*		
	At 0°C	*At 25°C*	*At 50°C*
10%	63.1%	64.8%	66.6%
20%	57.0%	58.5%	60.0%
30%	51.7%	53.3%	55.0%
40%	46.9%	48.4%	50.0%
50%	42.1%	43.4%	44.8%
60%	37.2%	38.5%	39.7%
70%	32.1%	33.1%	34.5%
80%	26.1%	27.2%	28.2%
90%	17.8%	18.5%	19.2%

According to Wilson, good concordance from 30–60% acid (or from 17–76% relative humidity) was obtained. The experiments on drying were carried out at humidities between 40% and 80%. From tests described below, the method worked quite satisfactorily under carefully regulated conditions.

The apparatus used is shown on Plate III. With the exception of the first and the last bottle, the entire apparatus including the humidifying bottles and the drying chamber was immersed in crushed ice contained in a well-insulated tank about 14 inches high and 20 inches in diameter. Air from the pump was first allowed to bubble through a more concentrated sulphuric acid solution to give it a preliminary dehumidification at room temperature. This step was very necessary, because air at ordinary temperatures on being chilled soon deposited moisture which froze in, and clogged up, the cooling coils. Without the dehumidifier, it was also difficult, to obtain low humidity. After the air had been dehumidied it was comparatively easy to recharge it with moisture at 0°C. The second bottle (b) served as a trap to catch any moisture that was left, and deposited it at 0° C. From there the air went directly to the copper cooling coils (c) about 20 feet

1. J. Ind. & Eng. Chem., *13*, 326 (1921).


TOP VIEW
PLATE III
DRYING APPARATUS FOR USE AT 0°C.
a = concentrated H_2SO_4 jar
b = moisture trap
c = cooling coil
d-h-p = safety bottles
e-f-g = H_2SO_4 solution bottles
i = main chamber
j-k-l = H_2SO_4 solution dishes
m = removable cover
n = one-holed stopper
o = wire gauze
r = rack
q = H_2SO_4 solution seal & bubble counter
air
ice
j-k-l
SECTION
EXTENDED VIEW

long, and then to the humidifying bottles (e, f, and g), each containing acid of given concentration, while *d* and *h* served as safety bottles to prevent any acid from going back to the copper tubing. The properly humidified air then entered the main chamber from the bottom through a perforated tube. The chamber was made of galvanised iron, about 1 foot high and 9 inches in diameter, provided with wire gauze near the bottom for the drying rack and a removable cap (or a large rubber stopper) at the top to facilitate the removal and replacement of samples. To insure proper condition of humidity and to maintain constant equilibrium inside the chamber, three or four crystallizing dishes containing acid of the same concentration were placed beside the rack. The air issued from the chamber, traveled through another safety bottle and escaped through the last acid bottle (not in the ice bath), which acted both as a seal and as a bubble counter. It was necessary to keep the air current at a definite speed (ascertained by trial) to effect the desired humidification and dehumidification and at the same time to prevent any stagnation of air inside the chamber.

The chamber was so constructed that larger plates could be used if desired but in this work those measuring 3″ x 2″ were found to be most convenient. After the plates had been in the chamber for a definite length of time, they were removed and placed in a dessicator to acquire room temperature before weighing. This transference was made as rapidly as possible, as exposure to atmosphere, even a short one, at once condensed some moisture on the plates, changing the humidity, and rendering the observation valueless.

The Test. The apparatus was tested in the same way as before, viz., by determining the amount of water present in a given volume of chamber air. At first, inconsistent results were obtained, due probably to one or all of the following causes: (1) the use of ordinary concentrated acid (about 95%) in the first bottle dehumidied the air so much that it did not pick up moisture readily in the later steps, (2) the concentration of the dilute acid being roughly determined by means of a hydrometer, was not exact, (3) the rate of flow was either too slow or too rapid, and (4)

equilibrium had not been established in the chamber. To eliminate these errors, the acid in the humidifying bottles and in the dishes was made up to exact strength (determined by titration against standard alkali), and that in the dehumidifying bottle of such strength as would give definite humidity at room temperature (25°C.) to correspond approximately to the desired humidity at 0° C., thus

Relative Humidity at 0° C.	*Corresponding R. H. at 25° C.*	*Acid used in 1st. Bottle*	*R. H. given at 25° C.*
40%	8.5%	70%	less than 10%
60%	13.4%	65%	10%
80%	17.1%	61%	15%
100%	22.4%	58.5%	20%

The air was allowed to pass through the system for at least 1½ hours before testing, at first rather rapidly for about 15 minutes to sweep out the air already in the chamber and then very slowly to give the proper humidification. The rate found most satisfactory in this work was from 100 to 125 cc. per minute. A number of tests were made for 40% and 80%, and the average was taken from two closest determinations. Better results were obtained after the above mentioned precautions were taken. Thus,

Volume of Air measured at 25° C.....18,000 cc.
Corresp. Vol. of Orig. Air at 0° C.....16,500 cc.

Test	*Total Moisture*	Av.	*Rel. Humidity Found*	*Sought*	*Error*
1	.0344 g	0.0356 g	44.5%	40%	-4.5%
2	.0368 g				
3	.0622 g	0.0652 g	81.5%	80%	-1.5%
4	.0682 g				

It will be seen that the error also decreased as the humidity increased, but the humidity actually obtained was greater than that sought.

(C) Procedure

The glass plates were thoroughly cleansed first with soap and water, then with pure water, and finally with alcohol. They were wiped dry with a clean towel, dried in a dessicator and weighed.

Prepared varnish mixtures were then applied to the surfaces as evenly as possible by means of a flat stiff brush, covering about the same area each time. Each plate was weighed again immediately after being coated. At first, it was thought that by using the same weight of the varnish for each plate, good results could be obtained. This, however, was not so. The great error due to rapid surface volatilization, resulting from manipulating the lacquer over and over to attain definite weight, was considerable, and the results from such attempts were poor. Besides, varnishes of different viscosities and different specific gravities differed very widely in thickness even if the weights taken were the same. As the percentage change of weight of the varnish during the process of drying depends on its thickness rather than its weight, and as it is almost impossible to coat the plates equally thick, it is best to use personal judgment in applying the brush and in weighing out the sample as rapidly as possible.

The reasons why glass plates were chosen are many. Wood warped in the moist chamber. Even hard wood absorbed some varnish, and no two pieces of the same wood absorbed it equally. Metallic plates, such as iron, were effected by moisture as well as by lacquer. Aluminum is light, but such metal may have catalytic action on the drying of lacquer and was not used. Canvas or cotton cloths stretched on a frame permitted even distribution of varnish, but owing to its rough surface, the quality of the film could not very well be studied.

To obtain an even and smooth varnish-film on a non-absorbing surface, glass plates were found most suitable.

Note:—The duplication of the number of a plate in the following experiments is due to the fact that the same plate when cleaned of the varnish from one experiment was used again for another experiment.

DISCUSSION OF EXPERIMENTAL DATA

Series of experiments were carried out, using the apparatus described in the previous chapter. After the coated plates had been in the chamber for a definite period of time, they were taken out and weighed. The results obtained are tabulated and discussed below. The change of weight was taken as the chief criterion for determining the progress of drying because this gave the most dependable information from the quantitative point of view. As a sort of qualitative guide, four arbitrary standards have been adopted and entered in the data sheet as follows :—

A.....just beginning to dry
B.....drying, but still very sticky
C.....very slightly sticky
D.....dry to touch

A short dash in the table indicates that there was no change in the weight compared with the previous period.

In most of these experiments, duplicate sets of samples were prepared and examined side by side. The values obtained for the same varnish under identical conditions were generally found to be of the same order of magnitude. In the tables, only the set that gave the most consistent results was given. Wherever an error was caused by accident, the weighing was omitted as indicated by a question mark in the table. Values within brackets indicated abnormal decrease or increase of weight due to some unexplanable causes.

EXPERIMENT 1

Drying at 25° C. and 40% relative humidity

Dry bulb 77.5° F.

Wet bulb 61.5° F.

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period *in 3 hrs.*	*at end of 7 days.*	Character of final film
246	0%	33.3	0	0	Poor
247	10%	43.5	0	0	Ditto
248	20%	44.9	0	0	Ditto
249	30%	40.3	0	0	Ditto
250	40%	34.2	0	0	Ditto
251	50%	34.9	0	0	Ditto
252	60%	49.7	0	0	Ditto
254	70%	42.0	0	0	Ditto
255	80%	38.3	.3	.3	Somewhat more homogeneous
256	90%	40.2	.2	.2	Ditto
257	100%	30.7	.5	.5	Ditto

EXPERIMENT 2

Drying at 25°C. and 60% relative humidity

Dry bulb 77.5° F.
Wet bulb 67° F.

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period (in days)									Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7	
222	0%	42.0	0	—	—	—	—	—	—	—	—	0	Non-drying
244	10%	47.6	0	—	—	—	—	—	—	—	—	0	Ditto
245	20%	54.7	0	—	—	—	—	—	—	—	—	0	Ditto
225	30%	45.5	0	—	—	—	—	—	—	—	—	0	Ditto
226	40%	47.8	0	—	—	—	—	—	—	—	—	0	Ditto
228	50%	42.4	0	0.42	—	—	0.94	+.24	—	—	—	+.47	Ditto
229	60%	56.0	1.15	1.30	1.44	1.88	0.72	—	+.29	—	—	+.29 (A)	Ditto
230	70%	69.3	1.97	2.32	2.50	—	2.50	1.25	0.55 (A)	—	— (B)	0.55 (C)	Ditto
231	80%	79.1	2.56	—	—	—	—	1.06	—	— (A)	—	1.06 (B)	Ditto, but least sticky
232	90%	47.1	4.18	4.30	4.43	4.18	3.54	2.90	—	—	—	2.52	Non-drying
233	100%	42.7	6.55	6.78	7.00	7.50	7.00	5.85	3.50	—	—	3.50	Ditto

EXPERIMENT 3

Drying at 25°C. and 80% relative humidity

Dry bulb 77.5° F.

Wet bulb 73.0° F.

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period (in days)									Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7
301	0%	65.6	.48	7.85	11.90	7.85	—	—	—	—	—	(D) 7.85	Non-drying
304	10%	59.0	0	—	—	—	—	—	—	—	—	0	Ditto
306	20%	62.2	0	—	—	—	—	—	—	—	—	0	Ditto
307	30%	71.2	0	—	—	—	—	—	—	—	—	0	Ditto
309	40%	64.2	.6	—	—	—	—	—	—	—	—	.6	Ditto
311	50%	53.0	1.1	1.5	—	—	1.0	—	—	—	—	1.0	Ditto
314	60%	55.8	1.4	1.9	2.1	—	—	—	—	(A) —	(B) —	2.1	Ditto, but glossy
316	70%	48.5	2.3	2.5	—	(A) —	(B) —	(C) —	—	(D) —	—	2.5	Second best, dry and glossy
318	80%	43.4	6.0	8.3	—	(A) 8.5	(B) 9.2	(C) —	(D) —	—	—	9.2	Best, glossy and dry
320	90%	50.1	7.6	8.8	9.2	(A) 9.4	(C) 10.3	(D) —	10.4	—	—	10.4	Third best, dry but less glossy
321	100%	44.9	14.5	15.4	—	15.6	15.8	(A) —	(C) 16.2	(D) —	—	16.2	Fourth best, dry but flat

EXPERIMENT 4

Drying at 25° C. and 100% relative humidity

In a chamber saturated with moisture

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period (in days)										Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7	
101	0%	104.1	0	—	—	—	+.3	—	—	+1.0	+1.4	+2.1	Non-drying, non-adhering
103	10%	89.3	0	0	+.3	+.7	—	—	—	—	—	+.7	Ditto
120	20%	106.4	0.3	0.4	0.5	—	+.1 (B)	+.3	(A) —	—	— (B)	(B) +.3 (C)	Homog., glossy, but sticky
121	30%	160.5	1.2	—	1.3 (A)	1.1 (B)	1.0	— (C)	—	—	—	1.0 (D)	Ditto
124	40%	80.9	1.25	—	—	.5	.5	.1	— (D)	—	—	0.1	Homog., glossy, and dry
125	50%	103.5	4.13	(A) 4.5	(B) —	(C) 3.8	3.4	—	—	—	—	3.4	Ditto
162	60%	110.0	(A) 8.0	(B) 8.2	(C) 8.3	(D) 7.5	7.1	—	—	—	—	7.1	Ditto
126	70%	96.2	(B) 10.4	(C) —	(D) —	9.5	9.2	—	—	—	—	9.2	Ditto, but less glossy
174	80%	82.0	(C) 11.5	(D) 10.8	10.3	—	9.4	—	—	—	—	9.4	Dull and opaque
167	90%	114.3	(C) 12.8	(D) 12.7	—	—	11.6	—	—	—	—	11.6	Ditto
198	100%	102.3	(C) 16.3	(D) 15.5	15.1	—	13.7	—	—	—	—	13.7	Dry, granular and rough

Discussion on Drying at 25° C

Experiments 1–4 were carried out at 25° C. with varying degrees of humidity. When the relative humidity was 40%, none of the samples showed even signs of incipient drying. In each case the appearance of the coating was poor, and the change of weight inappreciable. When the humidity was raised to 60%, varnishes containing 50% of lacquer or more showed an initial decrease of weight, reaching its maximum in 1–2 days after which the weight began to increase. None of the samples was dry at the end of seven days, but the general appearance was improved. At 80% relative humidity, several samples dried, 90% lacquer being the fastest, followed by 80%, 70%, and 100%. The change of weight in each sample, above 50% lacquer, was much greater, and the maximum change was reached in about 2–4 days. It is noteworthy that throughout the experimental period, there was a continual but gradual decrease of weight in every mixture,—a fact which was not observed under other conditions. This does not mean that the varnishes would lose weight indefinitely but rather that the maximum decrease was being reached much more slowly, perhaps many days after the samples were dry to touch. A careful examination of the data will show that this was true, for not a single value in this case exceeded the maximum decrease of weight (of the same mixture) in the other cases. Nor does the continual decrease indicate that there was only volatilization without oxidation. The films formed were glossy, tenacious and in most cases superior to those formed at other temperatures and humidities. There is, therefore, every reason to believe that oxidation has set in to make the net decrease of weight proportionally less. This, then, may be regarded as the optimum condition under which most high percentage lacquers dried, for at 100% relative humidity, although some did dry faster, the films formed lacked firmness and tenacity.

In general, 80% lacquer gave the best film at 25° C. Varnishes with higher percentages of lacquer gradually lost their lustre while those containing more oil decreased in hardness of film. It will be seen that the larger the lacquer content, the

greater the percentage loss of weight. This proves that the initial drying of lacquer is due *mainly* to volatilization. Oxidation which sets in after most of the volatile matter has escaped and after the film becomes apparently dry, only serves to strengthen and harden the film. This is indicated by the fact that the weight of the film steadily increased as the dried film became harder and harder.

The proportional loss of weight of most varnishes was greater at higher humidities, proving that lacquers do not absorb moisture to any appreciable extent, but form with it intermediate products which hasten the escape of the volatile matter originally present.

High percentage lacquers generally dried with a dull surface, due to too rapid volatilization. Addition of bodied wood oil in proper proportions, retarded the rate of drying to some extent, and thereby improved the gloss and tenacity of the film. Oxidation plays just as important part as volatilization. Pure bodied wood oil did not dry at all at 25° C., showing that this temperature is not favorable for the oxidation of wood oil.

EXPERIMENT 5

Drying at 40° C. and 40% relative humidity

Dry bulb 104° F.
Wet bulb 82° F.

No. of Plate	% of Lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period in days *in 3 hrs.*	*at end of 7 days*	(D)	Character of final film
239	0%	74.0	0.2		4.0	Dry, glossy and transparent
246	10%	40.7	0		0	Poor, non-drying
250	20%	36.3	0		0	Ditto
254	30%	62.0	0		0	Ditto
258	40%	40.0	0.3		0.3	Ditto
259	50%	50.6	0.7		0.7	Ditto
262	60%	45.6	0.9		0.9	Ditto
301	70%	64.6	1.5		1.5	Ditto
304	80%	62.4	1.6		1.6	Ditto
305	90%	69.6	2.3		2.3	Ditto
308	100%	34.0	2.5		2.5	Ditto

EXPERIMENT 6

Drying at 40°C. and 60% relative humidity

Dry bulb 104.0° F.
Wet bulb 90.5° F.

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period (in days)										Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7	
201	0%	81.4	0	—	—	—	+.9	+2.3	+3.7	—	+3.9	(D) +4.5	Dry and glossy
212	10%	71.9	0	—	—	—	—	—	—	—	—	0	Non-drying
228	20%	62.6	0	—	—	—	—	—	—	—	—	0	Ditto
241	30%	56.6	0	—	—	—	—	—	—	—	—	0	Ditto
249	40%	57.0	1.4	—	—	—	—	—	—	—	—	1.40	Ditto
262	50%	67.2	(3.26)	(8.0)	—	(9.2)	—	—	(8.60)	0	(7.35)	(6.66)	Ditto, abnormal weight decrease unexplanable.
301	60%	65.9	1.23	—	—	—	.76	—	.60	.44	+.33	(A) +1.06	Highest gloss, not dry
308	70%	49.4	2.20	—	—	—	1.20	(A) —	(B) .40	0	(C) +.6	+.7	Glossy, slightly sticky
311	80%	45.5	4.40	4.83	(A) —	—	4.17	(B) —	(C) 3.30	2.68	(D) 1.54	1.54	Driest of all (dull)
325	90%	43.8	4.32	—	—	—	—	—	(A) 3.70	3.90	(B) 2.28	(D) 2.28	Dry (dull)
327	100%	50.0	10.00	—	—	—	—	9.80	(A) —	9.90	(B) —	(C) 10.00	Not quite dry (dull)

EXPERIMENT 7

Drying at 40° C. and 80% relative humidity

Dry bulb 104.0° F.
Wet bulb 97.5° F.

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period (in days)									Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7
311	0%	81.4	0	—	—	—	+.61	—	(A) +3.07	(C) +6.0	+7.5	(D) +8.1	Transparent, not continuous.
314	10%	58.8	0	—	—	—	—	—	—	—	—	0	Non-drying
318	20%	66.8	0	—	—	—	—	—	—	—	—	0	Ditto
321	30%	62.2	0	—	—	—	—	—	—	—	—	0	Ditto
340	40%	69.1	2.9	—	—	—	—	—	—	.3	—	.3	Ditto
346	50%	69.5	1.1	—	—	—	1.3	1.1	.9	(A) .7	—	0	Ditto
350	60%	98.8	2.8	—	(A) —	2.4	(B) —	(C) 2.5	2.3	1.7	—	1.7	Still sticky, but glossy
352	70%	57.3	(2.1)	(A) —	(B) —	—	(C) (1.5)	—	(D) (1.0)	(0.3)	—	(0.3)	Next to 80%
354	80%	61.6	(A) 8.1	(B) 7.3	(C) —	7.1	(D) —	—	6.3	5.7	—	5.7	Most glossy and least tacky
356	90%	51.5	9.5	9.1	(A) —	(B) —	(C) 9.3	8.4	6.6	—	(D) —	6.6	Next to 70%
358	100%	64.3	19.9	19.3	—	(A) —	(B) —	(C) 17.3	16.3	—	—	(D) 16.5	Dries flat

EXPERIMENT 8

Drying at 40°C. and 100% relative humidity

Dry bulb 104° F.
Wet bulb 104° F.

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period (in days)										Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7	
324	0%	39.7	0	—	—	—	+.9	+2.5	—	+5.0	—	(D) +9.0	Dries uneven
326	10%	53.9	.4	—	—	—	—	—	—	—	—	0.4	Not dry
328	20%	68.2	.5	—	—	—	—	—	—	—	—	0.5	Not dry
329	30%	45.7	.6	.8	—	—	(A) —	—	—	—	—	(B) 0.8	Very sticky but glossy, homogeneous
331	40%	62.5	1.1	1.3	(A) —	—	(B) 0	—	—	(C) —	—	0	Less sticky, less glossy, homogeneous
334	50%	62.6	1.1	(A) —	(B) —	(C) —	.3	—	—	—	—	0.3	Ditto
336	60%	61.4	(A) 2.8	(B) —	(C) —	—	0	—	(D) —	—	—	0	Dry, glossy and homog.
338	70%	68.1	(B) 5.7	(C) —	—	(D) —	5.1	5.2	5.0	—	4.7	3.8	Ditto
340	80%	57.0	(B) 11.2	(D) —	—	—	11.1	—	11.2	11.0	10.9	9.8	Ditto
342	90%	58.5	(C) 12.0	(D) 12.5	12.6	—	12.5	—	—	12.1	12.0	11.3	Dry and flat
343	100%	37.8	(D) 19.8	—	—	—	17.6	—	—	—	—	16.0	Dry and flat

Discussion on Drying at 40° C

The results of Experiments 5–8 showed the behaviour of lacquer varnishes when dried at 40° C. With 40% relative humidity, only pure bodied wood oil dried in five days with a glossy and transparent film, gaining about 4% of its weight. The change in the other samples was hardly appreciable, although the decrease in weight was somewhat higher than at 25° C. with the same amount of moisture in the drying chamber. At 60% relative humidity, two samples (80% and 90% lacquers) which were found sticky at 25° C., dried with a dull surface. Pure lacquer remained sticky. As the humidity was increased, the varnishes dried more rapidly than at 25° C. But the film of pure wood oil gradually lost its homogeneity and tenacity, although it gained more weight. With this single exception, the decrease of weight was all followed by an increase, generally before the final drying took place. The film formed by 80% lacquer still appeared best in its physical properties.

In general, the dried films here showed a higher gloss, due evidently to the fact that the wood oil contained in the mixture dried better at higher temperatures. This gloss, as before, was best when the relative humidity was 80%. The only draw-back is that the films dried at 40° C. appeared softer than those dried at 25° C. Also they peeled off from the glass surface more easily when perfectly dry after long standing.

EXPERIMENT 9

Drying at 0°C. and 40% relative humidity

H_2SO_4 (in the dehumidifiers) 70% (corresponding to less than 10% R. H. at 25° C.)

H_2SO_4 (in the humidifier) 47%

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period in days *3 hrs.*	*at end of 7 days*	Character of final film
154	0%	105.2	0	0	Non-adhering, not dry, poor film
155	10%	59.4	0	0	Ditto
156	20%	85.5	0	0	Ditto
157	30%	94.9	0	0	Ditto
158	40%	96.0	0	0	Ditto
159	50%	100.0	0	0	Ditto
160	60%	104.0	0	0.6	Ditto
161	70%	91.4	0.2	1.1	Ditto
162	80%	67.8	1.0	1.5	Ditto
163	90%	75.9	2.3	3.8	Ditto
164	100%	95.8	4.7	5.3	Ditto

EXPERIMENT 10

Drying at 0°C. and 60% relative humidity

H_2SO_4 (in the dehumidifier) 65% (corresp. to 10% R. H. at 25° C.)
H_2SO_4 (in the humidifiers) 37.2%

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each Period (in days)									Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7	
25	0%	182.3	0	—	—	—	—	—	—	—	—	0	Non-drying
27	10%	100.0	0	—	—	—	—	—	—	—	—	0	Ditto
41	20%	98.1	0	—	—	—	—	—	—	—	—	0	Ditto
42	30%	109.3	0	—	—	—	—	—	—	—	—	0	Ditto
133	40%	114.3	1.3	—	—	—	—	—	—	—	(A) —	1.3	Ditto
134	50%	91.7	2.6	—	—	—	(A) —	(B) —	—	—	—	2.6	Very sticky
136	60%	105.9	6.2	—	—	(A) —	(B) —	—	(C) —	—	—	6.2	Sticky, but highly glossy
138	70%	123.0	3.9	—	4.2	(A) —	(B) 4.4	—	(C) —	—	—	4.4	Slightly sticky, less glossy than 60%
140	80%	95.4	5.2	—	(A) —	(B) —	(C) 5.3	5.6	(D) 6.0	—	—	6.0	Dry, but dull
143	90%	114.1	9.5	—	(A) 9.9	(B) —	(C) 10.5	(D) —	—	—	10.2	10.2	Dry, dull
144	100%	103.8	19.1	—	—	(A) —	(C) 21.6	(D) —	—	—	20.2	20.2	Dry, very dull

EXPERIMENT 11

Drying at 0°C. and 80% relative humidity

H_2SO_4 (in the dehumidifier) 61% (corresp. to 15% R. H. at 25° C.)

H_2SO_4 (in the humidifiers) 26.1%

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period (in days)										Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7	
176	0%	138.2	0	—	—	—	—	—	—	—	—	0	Non-drying
178	10%	95.1	0	—	—	—	—	–	—	—	—	0	Ditto
179	20%	88.9	0	—	—	—	—	—	—	—	—	0	Ditto
181	30%	107.5	0	—	—	—	—	—	—	—	—	0	Ditto
183	40%	89.7	0	—	—	—	0.2	0.9	1.56	—	1.11	1.11	Very sticky
185	50%	71.0	.28	.14	+.14	—	0	.56	(A) .85	5.6	—	.56	Sticky, but glossy
187	60%	105.7	.76	1.14	—	—	(A) —	(B) —	1.61	1.32	.76	.76	Sticky, less glossy
190	70%	152.2	3.28	4.14	(A) 4.47	(B) 4.60	(C) —	4.80	5.32	5.12	—	(D) 5.12	Dry, less glossy
192	80%	162.1	7.40	9.35	(A) 10.85	(B) 11.30	(C) 11.66	12.00	(D) 12.20	12.00	—	12.00	Dry, less glossy
193	90%	106.6	11.90	12.75	13.70	(A) 13.80	(C) 13.90	(D) 14.00	14.83	14.40	—	14.40	Dry, dull
195	100%	101.2	15.90	17.10	(A) 17.70	(B) 17.80	(D) 18.00	18.80	18.80	—	—	18.80	Dry, dull

EXPERIMENT 12

Drying at 0°C. and 100% relative humidity

H_2SO_4 (in the dehumidifier) 58.5% (corresp. to 20% R. H. at 25° C.)

Water (in the humidifiers)

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after each period (in days)										Character of final film
			3 hr.	6 hr.	½	1	2	3	4	5	6	7	
197	0%	116.1	—	—	—	—	—	—	—	—	—	0	Non-drying
199	10%	134.4	—	—	—	—	—	—	—	—	—	0	Ditto
201	20%	124.1	—	—	—	—	—	—	—	—	—	0	Ditto
204	30%	71.0	.3	—	—	—	—	—	—	—	—	.3	Ditto
205	40%	108.0	.46	—	—	—	(A) —	—	—	—	—	(B) .46	Ditto
207	50%	114.8	1.3	—	—	(A) 1.5	(C) 1.0	—	—	—	—	1.0	Still sticky
210	60%	133.0	3.0	—	—	(A) —	(C) 2.9	—	—	—	—	2.9	Sticky, but glossy
212	70%	122.6	8.2	—	(A) —	(B) —	(C) —	—	(D) —	—	—	?	Dry, less glossy than 60%
213	80%	102.6	11.2	(A) —	(B) —	(C) —	(D) —	10.0	—	—	—	10.0	Dry and flat
215	90%	86.8	(A) 11.6	(B) —	(C) —	(D) 12.1	11.7	—	—	—	—	11.7	Ditto
218	100%	63.5	(A) 18.5	(B) —	(C) —	(D) 19.0	—	—	—	—	—	19.0	Ditto

Discussion on Drying at 0° C

In order to find out how lacquer varnishes behaved in the cold days of winter, Experiments 9–12 were carried out. As usual, no samples dried at or below 40% relative humidity. When the humidity reached 60% lacquers with 80% and up dried much faster than at 25° C. or 40° C. This appeared to be the most favorable humidity at freezing temperature under which high lacquers dried. At still higher humidities, the film became more and more dull, although the rate of drying seemed faster.

Besides the dullness of the films, it is note-worthy that the coats which appeared perfectly dry when taken from the ice bath became stickly again on exposure to room temperature. This shows that drying at 0° C. is quite a different process. Volatilization here is followed by gelation (or congealing) which prevents further drying through oxidation. At warmer temperatures, the gel softens again and undergoes the usual steps of true drying. This is borne out by the fact that houses painted with lacquer varnishes in the winter almost invariably "sweat" for one or two summers to follow. That low temperature is not favorable for the oxidation (or true drying) of lacquers is well shown by the experimental data. In most cases, the maximum decrease of weight was quickly reached, after which there was generally a long standstill with very little subsequent increase.

The conclusion is that, while it is possible to produce the effect of apparent drying at zero temperature by varying the degrees of humidity, such a temperature does not give a satisfactory film that is highly glossy and permanently free from tackiness.

Summary of Results

(Experiments 1–12 Inclusive)

Percentage Loss of Weight during the Drying

(I=initial loss; M=maximum loss; F=final loss)

Temp.		0°C				25°C			40°C		
Rel. Hum.		40%	60%	80%	100%	60%	80%	100%	60%	80%	100%
Conc. Lacq.											
100%	(I)	4.7	19.1	15.9	18.5	6.5	14.5	16.3	10.0	19.9	19.8
	(M)	5.3	21.6	19.2	19.0	7.5	16.2	16.3	10.0	19.9	19.8
	(F)	5.3	20.0	18.8	19.0	3.5	16.2	13.7	10.0	16.5	16.0
90%	(I)	2.3	9.5	11.9	11.6	4.2	7.6	12.8	4.3	9.5	12.0
	(M)	3.8	10.5	14.8	12.1	4.4	10.4	12.8	4.3	9.5	12.0
	(F)	3.8	10.2	14.4	11.7	2.5	10.4	11.6	2.3	6.6	11.3
80%	(I)	1.0	5.2	7.4	11.2	2.6	6.0	11.5	4.4	8.1	11.2
	(M)	1.5	6.0	12.2	11.2	2.6	9.2	11.5	4.8	8.1	11.2
	(F)	1.5	6.0	12.0	10.0	1.1	9.2	9.4	1.5	5.7	9.8
70%	(I)	0.2	3.9	3.3	8.2	2.0	2.3	10.4	2.2	2.1	5.7
	(M)	1.1	4.4	5.4	—	2.7	2.5	10.4	2.2	2.1	5.7
	(F)	1.1	4.4	5.1	—	0.6	2.5	9.2	+.7	.3	3.8
60%	(I)	0	(6.2)	0.8	3.0	1.1	1.4	8.0	1.2	2.8	2.8
	(M)	.6	—	1.6	3.2	1.9	2.1	8.3	1.2	2.8	2.8
	(F)	.6	—	.8	2.9	.3	2.1	8.1	+1.1	1.7	0
50%	(I)	0	2.6	.3	1.3	.4	1.1	4.1	(3.3)	1.1	1.1
	(M)	0	2.6	.8	1.5	1.4	1.5	4.5	(9.2)	1.3	1.1
	(F)	0	2.6	.6	1.0	.5	1.0	3.4	(6.7)	0	.3

Notes:

1. The broken line encloses all varnishes that dried within one week.
2. (F) represents the final loss of weight *at the end of one week.*
3. Values enclosed in brackets show abnormality and are found inconsistent with the other values in the same vertical series.
4. Blanks represent values undetermined because of some accident.
5. The changes of weight at 40% relative humidity both at 25°C and at 40°C are inappreciable.
6. Varnishes containing 40% of lacquer or less practically suffer no change in weight.

The results obtained from these experiments are summarized in the above table, in which *I* represents the initial loss of weight of the varnish during the first three hours, *M* its maximum loss during the course of drying, and *F* its final loss at the end of seven days. The light broken line marks the zone which encloses all varnishes that were found dry to touch within the experimental period. Varnishes containing less than 50% of lacquer were not included in the table, because none of these seemed to dry, the change in their weight being inappreciable. A study of this table reveals many interesting facts.

In the first place, it shows that in the case of varnishes which dried, the percentage loss of weight was, in general, definite at the same temperature. Thus,

Concentration of lacquer	*Maximum loss of weight at* 0° C.	25° C.	40° C.
100%	about 19–21%	16%	20%
90%	about 12–14%	10–13%	9–12%
80%	about 10–12%	9.5–11.5%	8–11%

It will be noted that the figures in the same horizontal line do not differ very much, showing that even at different temperatures, the percentage loss of weight for a varnish dried under favorable conditions, has a constant value.

For the same varnishes lying outside the drying zone, with a few exceptions, the loss was considerably smaller (e. g., at 0° C. pure lacquer lost only 5.3% of its weight at 40% humidity as against 19% at higher humidity). Under such conditions, the maximum loss may never be reached; therefore, the varnish remained tacky indefinitely.

Values in the vertical column for 25°C decreased more slowly, showing that this temperature is more favourable for the drying of low percentage lacquers. Observations on the time required for the drying of such varnishes, as shown on one of the following tables, proved this to be true.

It will be seen from the table that there are a few pairs of values which are very close to one another but which are separated by the line, one value lying inside, and the other lying outside, the "zone of drying" This is accounted for by the fact that, because of the lack of an absolute standard for drying, it is extremely difficult to draw a line of demarcation between two

cases where the varnish does not show wide difference in the rate of drying. In such a case, the numerical values obtained by actual weighing seem to have more significance than the arbitrary standards chosen for determining the drying of the films.

Optimum and Critical Conditions

TABLE I

Time Required for Drying (in number of days)

Temp.	0°C				25°C				40°C			
Rel. Hum.	40%	60%	80%	100%	40%	60%	80%	100%	40%	60%	80%	100%
Lacquer												
100%	—	2½	2	1	—	—	5	6 h.	—	—	7	3 h.
90%	—	3	3½	1	—	—	2½	6 h.	—	7	5½	6 h.
80%	—	2½	3½	1½	—	—	3	6 h.	—	6	2	6 h.
70%	—	—	7	4	—	—	5	½ d.	—	—	3½	1 d.
60%	—	—	—	—	—	—	—	1 d.	—	—	—	4 d.
50%	—	—	—	—	—	—	—	4 d.	—	—	—	—
40%	—	—	—	—	—	—	—	7 d.	—	—	—	—
Pure Wood Oil	—	—	—	—	—	—	—	—	6	7	7	7

TABLE II

Optimum and Critical Concentrations (in % of lacquer)
(A—First to dry; B—last among those that dried)

Temp.	0°C			25°C			40°C		
Rel. Hum.	60%	80%	100%	60%	80%	100%	60%	80%	100%
Conc.									
A	100	100	100	—	90	80	80	80	100
B	80	70	70	—	70	40	90	100	60

TABLE III

Optimum and Critical Humidities (in % relative humidity)
(A—Humidity at which the varnish dries fastest;
B—Humidity at which the varnish no longer dries)

Temperature	0°C		25°C		40°C	
Relative Humidity %	A	B	A	B	A	B
Concentration						
100%	100	40	100	60	100	80
90%	100	40	100	60	100	80
80%	100	40	100	60	100	40
70%	100	60	100	60	100	60
60%	100	80	100	80	100	80
50%	100	80	100	80	100	80
40%	—	—	100	80	—	—

TABLE IV

Favorable and Unfavorable Temperatures
(A—Favorable; B—Unfavorable)

Relative Humidity	60%		80%		100%	
Temperature (°C)	A	B	A	B	A	B
Concentration						
100%	0	40	0	40	40	0
90%	0	40	25	40	40	0
80%	0	40	40	0	40	0
70%	—	—	40	0	25	0
60%	—	—	—	—	25	0
50%	—	—	—	—	25	0
40%	—	—	—	—	25	0

Note: These tables are based only on the rate of drying.

Discussion on Optimum and Critical Conditions

Tables I to IV were constructed for the purpose of facilitating a comparative study of the three conditions as effecting the drying of lacquer-varnishes. They were all based on the rate of drying obtained from the experimental data, no attempt being made to describe and compare the quality of the film dried in each individual case. This has been given before in each experiment, and will be briefly discussed again.

Some *general* conclusions may be deduced from these tables.

Table I shows that: (1) When the temperature remains constant, increased humidity favours drying.

(2) When the relative humidity remains constant, lacquer-varnishes dry better at 25° C. than at 0° C. or 40° C.

(3) Under the same atmospheric conditions, higher percentage lacquers dry faster than lower ones.

Table II shows that: (1) Higher percentage lacquers always dry faster,

(2) At 25° C. no lacquer dries with concentration below 40%
,, 40° C. none dries below 60%
,, 0° C. none dries below 70%

(3) At 100% Rel. Hum., none dries with concentration below 60%
,, 80% Rel. Hum., none dries below 70%
,, 60% Rel. Hum., none dries below 80%

Table III shows that: (1) Most lacquers dry in air saturated with moisture.

(2) Higher percentage lacquers require less moisture for their drying.

(3) 80% lacquer, as a special case, requires the least amount of moisture for its drying.

Table IV shows that: (1) Low temperatures are more favorable for drying at low humidities.

(2) When the atmosphere is saturated with moisture, higher lacquers dry better at 40° C. and lower ones dry better at 25° C.

Final Conclusions

As has been stated, these tables refer only to the rate of drying, without any regard to the quality of the film formed. In previous discussions, it will be remembered that 100% humidity, while hastening the drying of most lacquers, does not always give a satisfactory film. Elevated temperature seems to improve the gloss of the film, but it reduces its hardness and tenacity. At very low temperatures, many samples appear to dry fast, but the dullness of the film and the return of tackiness on exposure to ordinary atmospheric conditions, offer serious drawbacks. Pure lacquer always dries fastest, but the film is invariably flat. When everything is taken into consideration, it is concluded that *the most favorable condition for drying lacquers is at 25° C. with 80% relative humidity, and that the varnish which gives the most satisfactory results is the one containing 80% Chinese lacquer and 20% bodied China wood oil.*

EXPERIMENT 13

Drying at 0° C. and 0 % Relative Humidity

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after 3 hrs.	7 days	Character of final film
201	0%	81.4	0	0	Poor, non-drying
202	10%	70.0	0	0	Ditto
205	20%	23.8	0	0	Ditto
207	30%	38.3	0	0	Ditto
212	40%	50.1	0	0	Ditto
214	50%	61.2	0	0	Ditto
216	60%	75.7	0	0	Ditto
226	70%	44.7	.2	.2	Ditto
229	80%	32.8	.4	.4	Ditto
238	90%	53.4	2.5	2.5	Ditto
242	100%	50.8	3.8	2.8	Ditto

EXPERIMENT 14

Drying at 20° C. and 0 % Relative Humidity

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after 3 hrs.	7 days	Character of final film
201	0%	81.6	0.1	3.2	Poor, non-drying
202	10%	37.0	0	0	Ditto
203	20%	36.1	0	0	Ditto
204	30%	50.7	0	0	Ditto
205	40%	50.6	0	0	Ditto
206	50%	56.3	1.6	3.7	Ditto
207	60%	37.7	1.1	2.9	Ditto
208	70%	44.8	4.0	4.4	Ditto
209	80%	64.2	(11.2)	(9.0)	Ditto (least sticky)
210	90%	27.9	5.7	5.7	Ditto (more sticky than 80%)
211	100%	47.9	9.2	13.9	Ditto

EXPERIMENT 15

Drying at 40° C. and 0 % Relative Humidity

121	0%	157.2	0	+8.0	Dried in 7 days to a glossy film.
122	10%	110.2	.6	.6	Poor, non drying
123	20%	167.6	.6	.6	Ditto
124	30%	81.2	.6	.6	Ditto
125	40%	88.2	1.25	1.6	Ditto
126	50%	90.8	4.1	4.3	Ditto
127	60%	151.0	6.6	6.7	Sticky, fourth best
128	70%	122.2	7.8	8.0	Sticky, second best
129	80%	152.5	12.4	12.9	Sticky, looks best
130	90%	140.6	14.4	14.4	Sticky, third best
131	100%	96.4	17.4	18.5	Sticky, fifth best

EXPERIMENT 16

Drying at 60° C. and 0 % Relative Humidity

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after 3 hrs.	7 days	Character of final film
44	0%	34.7	0	+4.3	Dried in 5 days to a glossy film.
45	10%	33.1	+.9	+1.5	Poor, non-drying
20	20%	163.7	1.5	1.5	Ditto
62	30%	122.4	2.8	2.8	Ditto
28	40%	103.5	5.9	5.9	Ditto
63	50%	182.5	10.0	10.0	Ditto
65	60%	145.5	11.6	11.4	Sticky but glossy
184	70%	124.4	12.5	12.2	Slightly sticky, glossy
202	80%	145.4	19.7	18.8	Ditto
204	90%	158.4	23.3	20.2	Dried flat in 7 days
54	100%	33.3	?	?	Dried flat in 7 days

EXPERIMENT 17

Drying at 80° C. and 0 % Relative Humidity

30	0%	172.1	0	+5.5	Dried in 4½ days to a transparent film.
31	10%	169.0	.2	1.3	Poor, non-drying
32	20%	157.8	.45	1.0	Ditto
33	30%	171.8	.47	1.0	Ditto
34	40%	142.6	.42	1.05	Fair, very sticky
35	50%	167.9	3.5	1.9	Slightly sticky
36	60%	187.9	7.1	5.5	Dried most glossy in 3 days
37	70%	159.5	7.5	6.4	Dried less glossy in 2 days
38	80%	151.7	8.8	7.8	Ditto
39	90%	201.1	14.1	12.9	Dried least glossy in 1 day
40	100%	131.9	17.1	15.2	Dried flat in ½ day

EXPERIMENT 18

Drying at 100° C. and 0 % Relative Humidity

No. of plate	% of lacquer in wood oil	Wt. taken (in mg.)	Percentage loss of weight after 3 hrs.	7 days	Character of final film
21	0%	174.1	+4.4	+5.5	Dried in 18 hrs., uniform transparent.
11	10%	144.3	0.3	(+2.4)	Dried in 2 days, less uniform
12	20%	166.3	0.3	+4.3	Dried in 7 days
13	30%	86.2	0.3	+4.0	Still sticky
14	40%	108.8	0.3	+1.6	Most sticky of all
15	50%	140.5	1.4	1.1	Dried glossy in 2 days
16	60%	213.2	5.8	3.1	Dried glossy in 1 day
17	70%	217.9	7.1	4.6	Dried glossy in 18 hrs.
18	80%	206.9	8.2	5.6	Dried glossy in 12 hrs.
19	90%	145.5	?	?	Dried smooth in 12 hrs.
20	100%	112.8	12.0	9.3	Dried flat in 3 hrs.

Discussion on Drying at 0% Relative Humidity

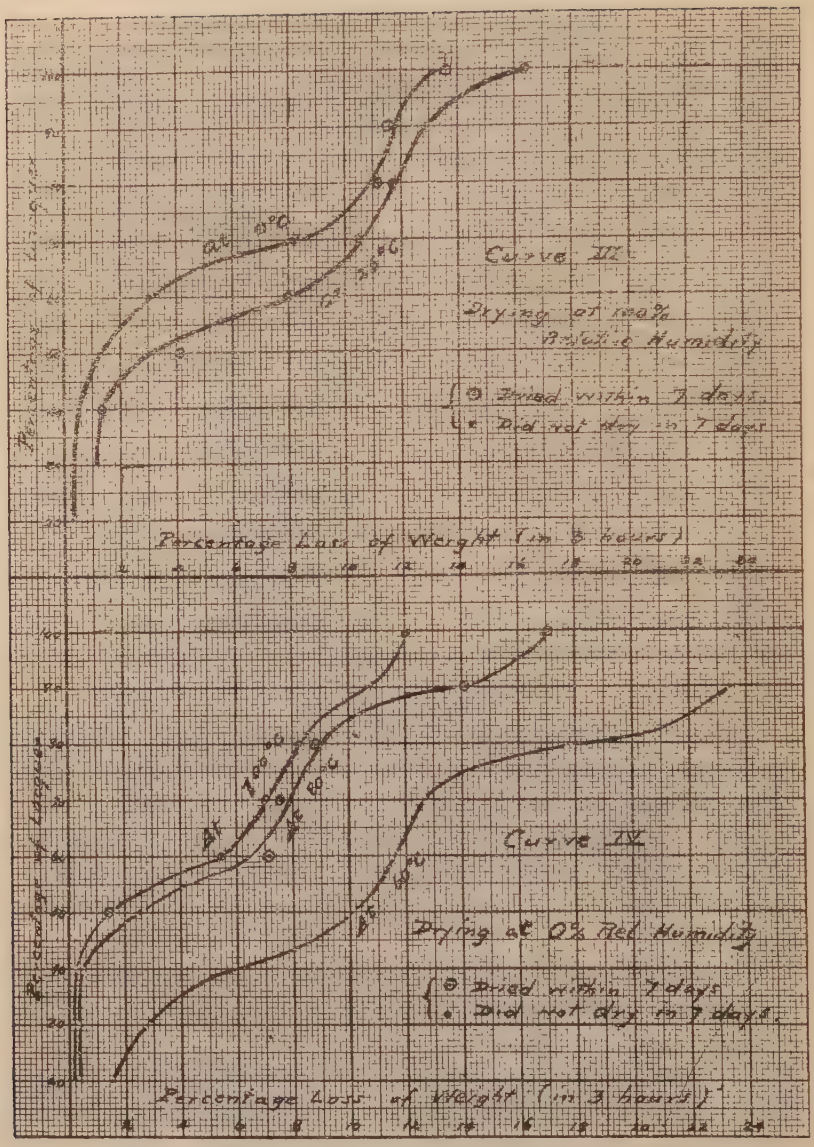
Experiments 13-18 were carried out to ascertain the behaviour of lacquer-oil varnishes when dried in the absence of moisture, over soda lime and $CaCl_2$ at 0°C to 100°C.

At 0°C, no samples dried. The change in weight was inappreciable, especially in the case of low percentage lacquers, showing that the temperature used was too low for volatilization as well as oxidation.

At 20°C, practically the same results were obtained. The decrease of weight was slightly greater, and the appearance of the coating was a little improved.

At 40°C, pure wood oil dried in 7 days with gain in weight. The decrease of weight in higher lacquers was still greater than at 20°C, but none of them dried free from tackiness.

At 60°C, pure wood oil dried with a good gloss in 5 days. 100% and 90% lacquers also dried. The change of their weight was considerable, being the highest decrease ever observed. This


Curve III
Drying at 100% Relative Humidity
Dried within 7 days
Did not dry in 7 days
Percentage Loss of Weight (in 3 hours)
Curve IV
Drying at 0% Rel. Humidity
Dried within 7 days
Did not dry in 7 days
Percentage Loss of Weight (in 3 hours)

showed that maximum volatilization took place at this temperature, with very little oxidation.

At 80°C, pure wood oil dried in 4½ days. Lacquers containing 60% or more, all dried with a gloss. The weight decrease was less than at 60°C, showing that dry oxidation had set in.

At 100°C, pure wood oil dried in 18 hours. Of the other samples, only the 30% and 40% lacquers were found sticky. The decrease of weight in the lacquers was still less than at 80°C. It is noteworthy that the drying here was approached from both ends, the rate of drying being slowest at the middle. This shows that dry oxidation was extremely active, effecting both the lacquer and the oil contained in it.

Examination of the experimental data and of the quality of the film formed, shows that the drying of lacquer-oil varnishes in the absence of moisture was quite different from the process through which ordinary drying was accomplished. No moisture was present as a catalyser (or oxygen carrier). No intermediate products or unstable hydrates were formed. All drying was done through straight oxidation and simultaneous volatilization. The dried films were mostly glossy, because the oil contained in them were likewise oxidised. Initial volatilization, therefore, gave little information with regard to the rate of drying. (The loss of weight at 60°C was much greater than at 80°C, and yet the samples did not dry so well).

The difference in the mechanism in the processes of drying may be best illustrated graphically by Curves III and IV. It will be seen that the shape of the curve is the same when the samples were dried at different temperatures with the same degree of humidity. In the absence of moisture, the slope on the upper branch of the curves changed, showing that the addition of wood oil to high percentage lacquers greatly hastens oxidation, making the net decrease of weight proportionally smaller. At the lower branch, the two curves almost coincide, because in samples containing much oil, the drying was done chiefly through oxidation whether moisture was present or not.

EFFECT OF DRIERS

The Effect of Driers on Lacquer-Oil Mixtures

The most common and almost the only drier used in China with lacquer is litharge. Miyama[1] in 1908 made a statement that ordinary driers blacken the lacquer and therefore cannot be used. This blackening, he asserts, likewise occurs when the lacquer is mixed with metallic powders or inorganic white pigments, and it is for this reason that the choice of colors is very limited. Nothing, however, was said about the rate of drying of lacquer or lacquer-oil mixtures as influenced by the addition of different kinds of driers, particularly the oil-soluble resinate-driers.

The following series of experiments were undertaken with a view of making a comparative study, in a general way, of the effect of some of the common driers on the drying of lacquer-oil mixtures, and also of the effect of concentration of one particular drier which seems to be the best promoter of drying.

Three typical driers were used :—

Name	*Metallic Content*	*Form*
Litharge	93% of Pb	Powder
Cobalt Linoleate	1.5% of Co	Liquid
Manganese Linoleate	2.43% of Mn	Paste

Carefully weighed amounts of each drier were added to lacquer-oil mixtures so that the resulting varnish contained 0.1% of the metal. In each case, whether the drier was a powder or a paste, it was first incorporated thoroughly with the oil used. Just enough heat was applied to dissolve the drier in the oil with gentle stirring. The oil containing the drier was then allowed to cool to room temperature as rapidly as possible. The required amount of lacquer was quickly added and trituated in a glass

1. J. Coll. Eng., Tokyo, *4*, 3; and Chemical Review, Fett-Harz-Ind., *15*, 148-9.

mortar for five minutes, care being taken to avoid oxidation through undue agitation. The resulting mixture was then turned into tin cans, covered with oiled paper (to prevent surface oxidation by air), and aged for one week before use.

A series of 12 samples of varnishes was thus prepared. Each sample was applied on a weighed glass plate (2″ x 3″) by means of a flat stiff brush as usual, placed on a rack, and dried in a chamber where air could freely circulate, but dust could not get in. The temperature was that of the room, about 22–25° C., and the relative humidity, as tested from time to time by the dry-and-wet-bulb method, varied between 65% to 75%.

After a certain number of hours, the coated plates were taken out and the weight of each was ascertained. The film in each case was examined, with special reference to color, tackiness, and homogeneity. As in the case of other experiments, the four arbitrary standards of drying were adopted throughout.

SERIES I — GENERAL DRIERS

No.	*Lacquer*	*Oil*	*Driers*	*Weight of Mixture Taken (1/10 mg.)*
155	70%	30%	None	1169
156	80%	20%	None	1096
157	90%	10%	None	1100
158	70%	30%	Lead Drier	1505
159	80%	20%	Lead Drier	1542
160	90%	10%	Lead Drier	1880
176	70%	30%	Cobalt Drier	1275
219	80%	20%	Cobalt Drier	1395
220	90%	10%	Cobalt Drier	1280
221	70%	30%	Mn Drier	1905
222	80%	20%	Mn Drier	1577
223	90%	10%	Mn Drier	1544

Decrease in Weight after Given Hours (in 1/10 mg.)

No.	*2*	*4*	*6*	*8*	*16*	*20*	*25*	*40*	*Hours*
155	24	44	...	...	...	...	...	41	
156	22	34	...	...	...	...	...	32	
157	25	26	...	...	...	...	...	...	
158	200	205	...	...	...	203	...	...	
159	225	229	...	...	...	...	...	...	
160	336	351	353A	...B	...C	354	...	...	
176	150	...	...	...	...	...	...	...A	
219	196	197	...	...	...A	...	...B	195	
220	170	171	...	...A	...B	169C	...	167	
221	269	281	282A	283B	...C	...	...	...	
222	232	248A	...	249B	247C	245	...D	...	
223	253	261A	262B	263C	260D	257	...	...	

Decrease in Weight (in 1/10 mg.) Continued

No.	*50*	*70*	*100*	*150*	*200*	*300*	*400*	*500*	*Hours*
155	...	...	...	...	...	...	...	41	
156	...	...	...	...	...	...	...	32	
157	...	52	...	65	...	...	...	65	
158	...A	...	...B	200	198C	...	192	192D	
159	...A	...B	...	...	227C	...	223	223D	
160	...	...D	...	352	...	...	349	348	
176	...B	...	...	140	...C	...	...	140	
219	...	...C	...	...	...D	...	193	191	
220	...	...D	...	...	166	162	...	160	
221	...	...D	282	280	279	...	274	264	
222	...	...	...	241	...	...	235	229	
223	...	...	...	254	...	...	253	247	

It will be seen from the above that all three driers promoted the drying of the varnish to an enormous extent. Most of the weight changes occurred during the first four hours, after which the change was exceedingly slow. In most cases, the maximum change in weight immediately preceded the final drying, after which the weight continued to increase very slowly.

NOTE: No change in weight over the previous period is indicated by short dashes in the table.

It will be noticed that in promoting initial drying, manganese was the best, cobalt next, and lead last. In aiding final setting, manganese came first followed by lead and cobalt. Cobalt did not seem to act well with mixtures where the oil content was high.

The character of the films after the end of the experiment was carefully observed. Those without driers remained "wet." All the rest were perfectly dry to touch, except one, viz., cobalt drier with 70% lacquer. Lead gave a brown film, glossy, tenacious and homogeneous. The cobalt films were also glossy, greenish to transmitted light but black to reflected light. Manganese films were perfectly black, opaque and were somewhat duller in appearance. This was generally the case when the lacquer varnishes dried too fast. The higher the lacquer content, the darker the film. This was to be expected, as lacquer itself when oxidised in air turns black.

It was found by this experiment that instead of depending on physical examination of the film alone, it is possible to determine the comparative accelerating power of the different driers from the quantitative results. Assuming that the initial drying is due mainly to volatilization from the lacquer contained in the varnish, the loss of weight divided by the percentage of lacquer gives a number which might be called the "volatilization factor." Here, of course, the loss of weight must be expressed in terms of 1/10 mg. loss per unit weight. In the following table, 150 mg. was taken as the unit weight of sample used.

No.	Loss of Wt. (*per 150 mg.*)	Divided by	Volatilization Factor
155	31	.70	44
156	30	.80	38
157	34	.90	38
158	200	.70	285
159	219	.80	274
160	268	.90	298
176	176	.70	252
219	211	.80	263
220	199	.90	221
221	212	.70	303
222	236	.80	295
223	246	.90	273

It will be seen from these calculations that all the three driers promoted drying to about the same extent, viz., 6 to 8 times. The figures also show that manganese drier was the best of the three, while cobalt was poorest. This agreed very well with observed facts.

Attention was next drawn to the question : To what extent will the concentration of a drier influence the drying of the varnish with which it is incorporated? To find out this, manganese linoleate, which had been found by the first experiment to be the best promoter, was used in varying proportions, from 0.05% to 0.25% calculated from the active metal present. In order that the course of drying could be slowly and carefully followed at every stage, 70% lacquer was used and the varnish aged only for three days instead of one week. Otherwise, the method of preparing varnishes was exactly the same as the first series. Duplicate plates were prepared and dried simultaneously for checking. The results are tabulated as follows :—

SERIES II — MN DRIERS

No.	Conc. of Drier	Wt. of Sample Taken	Decrease in Wt. after given time (in 1/10 mg.)					*Hours*
			2½	*5*	*10*	*15*	*20*	
27	.05%	1640	266	267	...A	268	271B	
119	.05%	1513	204	205	...A	207	...B	
104	.10%	1243	176	179	...	180	185A	
105	.10%	1363	185	...	...	...	189A	
154	.15%	1925	292	295	...	...	300	
161	.15%	1239	182	184	...	...	187	
168	.20%	1512	207	207	218	209	218	
199	.20%	1600	239	242	...	...	245	
200	.25%	1175	140	149	...	153	...	
201	.25%	1275	142	141	155	159	...	

Decrease in Weight after Given Time (in 1/10 mg.)

No.	*40*	*60*	*80*	*100*	*150*	*200*	*300*	*Hours*
27	...	...	...C	...	...	270	264D	
119	...	...	...C	...	...	206	198D	
104	...B	...	...	...C	184	182	175D	
105	...B	...	188	...C	186	185	178D	
154	...A	...	...B	...	297	286C	286D	
161	...A	...	...B	...	185	...C	185D	
168	...	...A	...	...B	216	211C	201D	
199	...	...A	...	...B	241	238C	231D	
200	...	...	...	...	...A	151B	147D	
201	...	...	...	...	157A	150B	145D	

It will be seen that all samples were dry to touch at the end of 300 hours, except those containing over 0.20% Mn which still remained tacky. While the initial drying (A) was faster in the case of low concentration driers, the final setting (D) was reached about the same time. When the concentration of the drier exceeded 0.20%, the drying was slower and the film remained tacky after a long time. It was evident that there was a turning point somewhere around 0.20% beyond which the Mn acted as a retarder rather than a promoter. This may be explained by the fact that when the drier is in excess, a film is quickly formed on the surface, however thin and invisible it may be, which prevents further escaping of volatile matter. This was evidenced by the *small* percentage decrease in weight in the last sample.

As in other cases, the film that dried slowly assumed a more shining lustre. After the maximum weight-change was reached, the weight began to increase very gradually and continuously even after the films were apparently perfectly dry. It is probable that after very long exposure under exactly same conditions, the net proportional change in weight will be the same. No simple ratio had been found to exist between the net change (amount volatilized minus amount absorbed) and the amount of varnish taken. This depends upon the thickness of the film, the evenness of the coating, the method of applying the varnish, the cleanness of the surface to be coated, and many other factors ; a slight alteration of any one of these factors will enormously effect the rate of drying. Fluctuations of weight at a few periods suggested also that some unstable substance was being constantly formed and decomposed.

As was done before, the comparative accelerating power of Mn at various concentrations may be calculated from the "volatilization factor." This gives the following values :—

No.	Loss of Wt. (*per 150 mg.*)	Divided by Percentage	Volatilization Factor	Mean.
27	245	.70	348	318
119	202	.70	288	
104	214	.70	306	300
105	205	.70	293	
154	228	.70	326	321
161	221	.70	316	
168	205	.70	293	306
199	224	.70	320	
200	179	.70	256	247
201	167	.70	238	

The low "volatilization factor" of the .25% drier sample accounted for the slow drying and tackiness of the varnish film. This factor is about the same in the case of all the other samples. They should produce films of about the same quality. Experiment proved this to be true.

Conclusions on Driers

The experiments on driers showed :

(1) That lead, cobalt, and manganese driers, at same concentrations, accelerate the drying of lacquer-varnishes to about the same extent, Mn being slightly better,

(2) That, when the same drier is used at various concentrations, there is an optimum concentration which will produce the best film effect and beyond which the drier will act as a retarder rather than a promoter. This optimum concentration in the case of manganese drier used with 70% lacquer varnish seems to lie somewhere near 0.2%, and

(3) That the comparative power of acceleration of driers may be measured by the "volatilization factor," a number obtained by dividing the loss of volatile matter per unit weight of sample during the first two hours by the percentage of pure lacquer present in the varnish.

III. CONCLUDING PART

SUMMARY OF EXPERIMENTS AND CONCLUSIONS

The results from organic combustion and molecular weight determination showed that the lacquer used in this research was of the same kind as used by Majima, Miyama, and other investigators.

The experiments on viscosity showed that the mixture of Chinese lacquer with China wood oil results in emulsification, and that the optimum concentration is the mixture which gives the most complete emulsification.

The experiments on drying showed :

(1) That 25°C is a more favourable temperature than 0°C or 40°C for the drying of most lacquer-oil varnishes ;

(2) That 80% relative humidity is the optimum humidity under which to obtain the best results in the formation of the film ;

(3) That 80% lacquer and 20% wood oil is the optimum concentration, both regarding rate of drying and the quality of film ; and

(4) That lacquer-oil varnishes may also be dried in the absence of moisture at elevated temperatures, but the mechanism of drying in this case is quite different from that of drying when moisture is present.

The experiments on driers showed that Pb, Co, and Mn driers all accelerate the rate of drying to *about* the same extent and that the optimum concentration of the Mn drier (which is a better promoter than the other two) is somewhere around 0.2% (of the active metal.)

THE MECHANISM OF LACQUER DRYING

There has been no adequate theory presented covering the drying of lacquer-varnishes, but the drying process of "drying oils" which are probably related to such varnishes, was said by Hans Woulff[1] to consist of three stages: (1) oxidation with formation of a colloidal solution, (2) gel formation, and (3) further oxidation and ageing. The escape of volatile matter in the "drying oils" does not seem to play a very important part.

The process under which lacquer-oil mixtures dry is not exactly the same as that of "drying oils," and, moreover, the mechanism seems to vary with varying conditions.

(*1*) *In presence of moisture:*

At ordinary temperatures, the initial drying of pure lacquer or of lacquer-varnishes is always preceded or accompanied by a considerable loss of weight, showing that during the first stage of drying, vaporization of volatile matter in the lacquer is a very important factor. Oxidation at this stage seems rather insignificant compared with volatilization. That the loss of weight is greater at higher humidities shows that moisture hastens volatilization by the formation of some intermediate transition product (probably in the form of an unstable hydrate) of higher volatility. This is further substantiated by two facts. First, during the course of drying, the weight was found to fluctuate within small ranges at intervals. Secondly, in the practice of preparing raw lacquer in China, it has been found that the addition of a small quantity of water to the sap greatly aids evaporation, and that the resulting lacquer possesses better drying properties.

After the maximum decrease is reached, the weight generally begins to increase before the film "sets." This shows that, during

1. Chem.—Ztg., Dec. 4, 1924, pp. 897–9.

the second stage of drying, oxidation takes an active part. Its action is a gradual and a continual one, the film becoming harder as the amount of oxygen absorbed is greater. This setting is also accelerated by moisture, which seems to serve a double purpose here: (a) It acts as a catalytic oxygen carrier, and (b) it furnishes a good medium for the thriving of "laccase," which is an oxidase enzyme present in the lacquer. The importance of this enzyme has long been recognised by early investigators, and confirmed by the experimental facts in this research. The alcohol-soluble extract of lacquer, being deprived of all "laccase" and containing practically no nitrogen, did not dry at all, even after long exposure. According to Yoshida, the combination of oxygen and moisture at 20°C or thereabouts is an essential condition for the full display of the activity of the enzyme, and the enzyme ceases to be active above 63°C. The results of the present research further showed that 80% relative humidity at 25°C is the most favourable condition for such activity, for the best results were obtained under that condition.

When pure lacquer dries, especially when it dries very fast, it always results in a "flat" surface. Sometimes the film even peels off by curling up. This may be due to the shrinkage of the outer surface-film formed by rapid volatilization and rapid oxidation. The addition of a little bodied wood oil prevents rapid surface drying, and permits the complete oxidation of the sub-layer. The initial loss of weight will then become smaller while the final gain becomes greater. The wood oil, which permanently remains in the varnish and which is itself oxidized, imparts a glossy appearance to the film.

At lower temperatures, the initial loss of weight through volatilization is likewise considerable, due to the rapid formation of transition products with the moisture in the chamber. This is immediately followed by two actions: (a) Excessive cooling causes the varnish to congeal, and (b) a thin film which is rapidly formed at the surface prevents further oxidation of the under layer. True drying, therefore, can not be accomplished. The surface remains dull, and the film becomes sticky again on exposure to ordinary temperature. At this temperature, too, the oxidase

enzyme seems to lie dormant, and oxidation is therefore extremely slow. This is shown by the fact that there is but a small increase in weight after the maximum decrease is reached.

At higher temperatures, such as 40°C, the initial loss of weight is even greater, due to the free escape of volatile matter. After passing the point of maximum decrease, the weight increases very rapidly, showing that oxidation is here hastened by the combined action of heat, moisture, and the laccase, which latter, as mentioned above, is active until the temperature is 63°C or above. The high gloss of the film formed by the lacquer-oil mixtures shows that the wood oil in the varnish is more completely oxidized at this temperature. The reason why the films of higher lacquers often peel off has been given above.

(2) *In absence of moisture:*

When no moisture is present to act either as a catalytic oxygen carrier or as a favourable medium for the laccase to display its activity, the drying of the lacquer-varnish will have to depend chiefly on straight oxidation by dry air, which should closely follow the escape of volatile matter. At temperatues below 60°C, there is much volatilization and little oxidation. Consequently, the varnishes do not dry. At higher temperatures, the initial decrease of weight appears smaller, because oxidation has set in to partly offset the loss through volatilization. The films, therefore, dry with a good gloss. The most notable fact about this drying is that there is no evidence of the formation of an intermediate transition compound. The weight either steadily decreases, or steadily increases, with practically no fluctuations at intervals. Heat is the only agency in this case to aid the drying.

Summary:

To sum up, the drying of lacquer-oil varnishes in the presence of moisture is accomplished by (1) initial volatilization, (2) formation of intermediate transition compounds, and (3) final oxidation, all of which are accelerated by the action of moisture and enzyme. In the absence of moisture, the varnishes dry through straight oxidation following volatilization, and this is aided by heat.

GENERAL SUMMARY

1. A systematic study has been made on the drying of lacquer-oil varnishes under varying conditions of temperature, humidity, and concentration.

2. An optimum condition has been found with regard to temperature.

3. An optimum condition has been found with regard to humidity.

4. An optimum condition has been found with regard to concentration.

5. A scientific basis has been discovered for the mixing of lacquer with wood oil.

6. A reason has been found to explain the difference in the mechanism of drying under different conditions.

7. An optimum concentration has been found for driers.

8. A new apparatus has been devised whereby the relative viscosity of all varnishes in general may be measured with reasonable degree of accuracy, within wide ranges.

9. A new apparatus has been devised whereby the drying of varnishes may be accomplished at ordinary temperatures with varied degrees of humidity under absolute control.

10. A new apparatus has been devised whereby the drying of varnishes may be accomplished at zero temperature with varied degrees of humidity under absolute control.

VITA

Zai-Ziang Zee (徐善祥) was born in Shanghai, China, Dec. 10, 1882. He received his education in Chinese under a private tutor at home. He passed the Prefectural Competitive Examination in 1898, receiving the degree of Bachelor of Literature (in Chinese). After that, he studied English in St. John's College, Shanghai, and was graduated from the Collegiate Department of that Institution in 1904. He taught in Nanyang High School, Shanghai, for two years; entered Yale University, New Haven, in the fall of 1906; and was graduated there 1909, with the degree of Bachelor of Philosophy. After one year's research work on pyrimidines, he returned to China in 1910 to serve as Director of Studies in the National Academy, Woosung. From 1911 to 1913, he edited a number of scientific textbooks both in Chinese and English, most of which were published in the Commercial Press, Shanghai. During 1914 and 1915, he served in the Ministry of Finance, Peking, as Government Assayer in the Department of Mints. Beginning from the fall of 1916, he joined the staff of Yale-in-China, Changsha, as head of the Deparment of Chemistry. Leaving Changsha on furlough in the fall of 1923, he resumed his studies in chemistry in the U. S. A., as a Research Fellow of the Rockefeller Foundation. After pursuing graduate studies in Yale for one year, he entered Columbia University in July, 1924. Since then, he has been doing research work in the Department of Chemical Engineering.